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THE

# PHYSICAL REVIEW.

## RESISTANCE AND THERMO-ELECTRIC POWER OF METALLIC GERMANIUM.[1]

By C. C. Bidwell.

Synopsis.

*Electric Resistance and Thermo-electric Power of Germanium, from −191° to 675° C.*—Measurements were made on a pure specimen of this rare metal in the form of a rod 2.4 by 0.44 by 0.41 cm., prepared under the direction of L. M. Dennis. The current was led in through graphite blocks and thermo-junctions were placed in grooves near each end. For the thermo-electric power determinations a temperature gradient was secured by placing the specimen in a non-uniform part of a furnace or refrigerator and also by using a heater coil wound on one end. Between 125° and 450° the results indicate a slow reversible transformation of some sort, for below and above this range the thermo-electric power is a linear function of the temperature and also, except in the range 100° to 600°, the resistance is an exponential function of the form $\log R = \log A + aT + Q/kT$. The specific resistance reaches a minimum at −116° and again at 645°, the temperature coefficient changing from positive to negative with rising temperature. Its value at 0° is 0.089 ohm per cm. cube.

*Periodic Relations among the Elements with Reference to Temperature Variation of Resistance* are pointed out. High resistance elements toward the right side of the Periodic Table have characteristically negative coefficients while the good conductors toward the left side have positive coefficients. The elements in Group IV, C, Si, Ti, Ge and Zr show transitional behavior, each giving indications at least of a minimum resistance at temperatures which decrease regularly from very high for the lightest to very low for the heaviest element.

*Transformation in Germanium, 125° to 450° C.*, as indicated by the above data, shows no hysteresis, the rapid cooling curves duplicating the slow cooling and heating ones. The phases are always in equilibrium, one, perhaps, being dissolved in the other.

THE production of a considerable quantity of pure metallic germanium under the direction of Professor L. M. Dennis, of the Department of Chemistry of Cornell University, has afforded an opportunity of studying the physical properties of this rare metal. Measurements of electrical resistance and thermo-electric power over a consider-

[1] The investigation upon which this article is based was supported by grants from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

able temperature range have been completed. The data are here shown graphically and discussed in connection with the position of germanium in the Periodic Table.

## PREPARATION AND METHOD OF STUDY.

The germanium was originally prepared from chemically and spectroscopically pure germanium oxide by reduction with hydrogen in an electric furnace. The powdered metal was then fused under sodium sulphate and the solid mass obtained again powdered and boiled in dilute hydrochloric acid. It was then again melted in hydrogen. Very carefully taken spectra showed no lines except those of germanium. The sodium lines were especially looked for but were entirely absent. With the above treatment there is little likelihood that the metal contained oxide. This view is strengthened by the melting point determinations which gave 958.7° C. agreeing with the value previously found by Biltz[1] for oxide-free germanium. Biltz showed that with germanium containing small amounts of oxide a reduction of several degrees in the melting point occurred. His highest value for material treated as above and melted in hydrogen was 958 ± 5.0. Professor Dennis sets the purity as better than 99.9 per cent.

The specimen as received was in the form of a rod, 2.4 cm. long, 0.44 cm. wide, and 0.41 cm. thick. Junctions of platinum and platinum-10 per cent. rhodium were first placed in grooves filed into the bar near each end and were bound into tight contact with the germanium by means of fine platinum wire. The specimen was then placed between two small blocks of graphite which were held by springs tightly against the

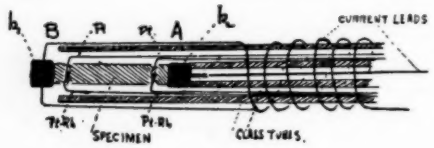


Fig. 1.

ends. Fig. 1 shows the arrangement. ($b_1$) and ($b_2$) are the graphite blocks through which current was led to the specimen. The block, ($b_2$), was pressed against the specimen by the glass tube through which one of the leading-in wires was passed. The block, ($b_1$), was pressed against the other end of the specimen by the tension of the other leading-in wire which was coiled as a spring around the glass tube, above mentioned, stretched and hooked into the far end of the tube. The leading-in wires were of nickel. The junction wires of platinum and platinum-

[1] W. Biltz, Zeit. f. Anorg. Chemie, 72, 313 (1911).

rhodium were led back along the tube, carefully insulated from one another and from the leading-in wires. The whole was enclosed in an outer glass tube. All the glass was pyrex.

Resistance was determined by sending current through the specimen, measuring the potential difference across the platinum wires as potential leads, and comparing the readings so obtained with the potential difference across a standard 1.0 ohm resistance placed in series. Measurements were made in this way in the following constant temperature baths: fresh liquid air (− 191° C.); old liquid air (oxygen) (− 183° C.); diethyl ether at its melting point (− 116° C.); carbon dioxide snow and ether (− 79° C.); freezing chloroform (− 65° C.); melting ice (0° C.); room temperature (+ 24° C.); and the following boiling points, chloroform (+ 61.2° C.), ethyl alcohol (77.5° C., with bar. at 736 mm.), water (98.9° C., with bar. at 732 mm.), anilin (183° C.), naphthalene (218° C.), benzophenone (305° C.) and sulphur (443° C., bar. 739 mm.). The temperature of the fresh liquid air was determined by extrapolation with a steel-constantan thermocouple, for the calibration of which liquid air four days old was taken as − 183° C. This temperature was indicated by a pentane thermometer originally calibrated by the Reichsanstalt. The resistance values obtained in the above baths are shown on the curve as points surrounded by circles. The specific resistance at zero Centigrade was found to be 0.089 ohm per cm. cube.

For thermo-electric power determinations it was necessary to establish a temperature gradient along the specimen, and then get the temperature at the point of contact of the platinum with the germanium near each end by means of the attached thermo-junction and to measure the electromotive force between the platinum leads when the specimen was on open circuit. The e.m.f. divided by the temperature difference gave the thermo-electric power for the mean temperature. For high-temperature determinations the specimen was placed in a vertical tubular furnace closed at the top with admission through the bottom. By adjusting the distance the specimen projected into the furnace any desired temperature gradient could be obtained. A heater coil of four turns of "chromel" wire wound on an asbestos tube and slipped over the specimen at *A* permitted of a reversal of the gradient when desired. Gradients varying from 5 to 60 degrees across the specimen were employed. Resistance measurements also were obtained under the same conditions. The large thermal e.m.f. was corrected for by reversing the current. The resistance values so obtained were assigned to the mean temperature and were found to fit exactly the curve obtained with constant temperature baths. Thus intermediate resistance points were obtained and likewise points beyond

the sulphur point as far as 675° C. It is to be noted that resistance values were obtained which may be regarded as simultaneous with the thermo-electric power data.

For data below room temperature, the platinum, platinum-rhodium couples were replaced by steel-constantan junctions, since the platinum couple is unsatisfactory for low temperature determinations, and the specimen was lowered into a long Dewar cylinder containing liquid air. Any temperature down to liquid-air temperature could be obtained sufficiently steady for satisfactory readings by merely adjusting the height of the specimen above the liquid air. By means of the heater coil the desired gradient could be maintained. The thermo-electric power against constantan was corrected to platinum.

## THE THERMO-ELECTRIC POWER LINE.

In the nature of the problem there always must be some uncertainty as to the actual temperature of the material at the point of contact with the junction wire. Exactly how closely the junction gives this temperature is open to question. It was originally hoped to thread the junction wires through very fine holes drilled through near each end. Germanium, however, is extremely hard and very brittle and no impression whatever could be made on the material with a drill. In spite of the uncertainty in respect to actual temperature the data certainly give the course of the thermo-electric power with fair accuracy. The thermo-electric power line shown represents the mean of several runs. Three runs were made using the heater coil which produced a thermal gradient down the specimen, *i.e.*, from *A* to *B* (Fig. 1), and two runs in which the heater coil was removed and a gradient established by the furnace in the opposite direction, *i.e.*, from *B* to *A*. The first three runs gave a curve which repeated itself very accurately. With the gradient reversed a slightly different curve was obtained which also was accurately repeated. Analysis of the conditions shows that the correct curve must lie between these two.[1] The line shown represents the most probable values of the thermo-electric power being the mean of the two sets of data.

[1] With the heat flow from *A* to *B* the junction at *B* must be heated from the specimen and therefore must be at slightly lower temperature than the specimen. If the heat flow is largely from the carbon block ($b_2$) into the specimen, the junction at *A* will also be at a lower temperature than the specimen. The heat flow at *A* was more nearly laterally inward since the heater coil was adjusted very nearly over the end of the specimen. The junction at *A* would thus be slightly warmer than the specimen. Thus the error at each end was in such a direction as to make the gradient appear larger than it actually was and to make the computed thermo-electric power too small. With the gradient in the other direction the heat reaches the specimen by way of the graphite block ($b_1$) and the junction at (*B*) is heated from the specimen. At (*A*) we have more nearly temperature equilibrium with the surroundings, therefore the discrepancy and between the temperature of the specimen that of the junction

The thermo-electric power line is straight from liquid-air temperatures up to about + 125° and again straight from 450° to 700°. Between these temperatures a transformation of some sort is shown by this line and also by the resistance curve. The transformation is a slow reversible one beginning at about + 125° and reaching completion at about 450°. Its completion apparently depends only upon the temperature and in no way upon the time. A careful study was made of this point as a result of a suggestion that if the changes were made more slowly the thermo-electric power line would be steeper in the transition region or if the temperature were held constant at some point in the transition region the change would progressively continue until all the material was in the second state. In this case the thermo-electric power line should

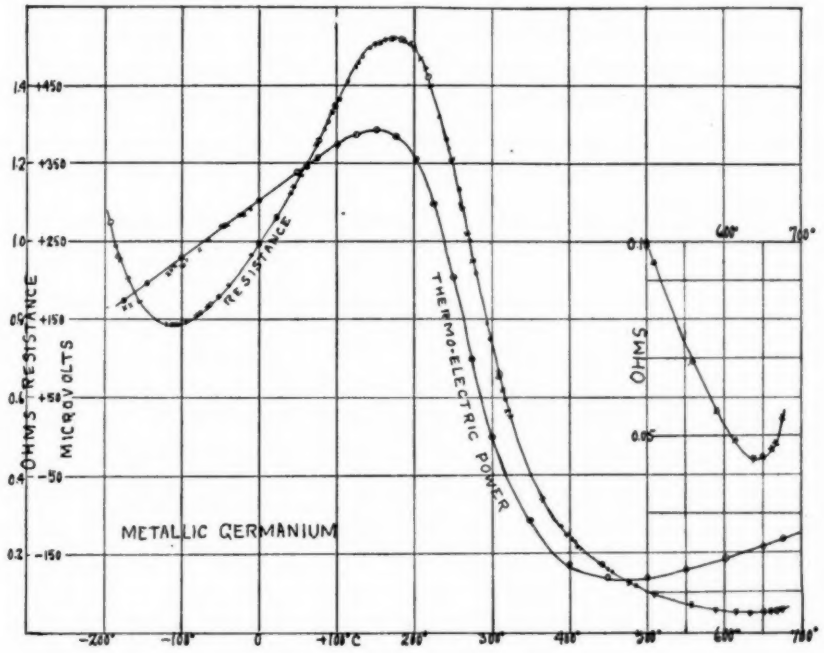


Fig. 2.

is not so great. The effect in this case is to make the observed gradient too low and the computed thermo-electric power too great. The per cent. variation from the mean was found to depend upon the temperature gradient, the per cent. error being less with larger gradients. In the region of 100°–200° where the gradient maintained was about 10°–15°, the per cent. variation from the mean was as high as 7 per cent. Above 400° where a gradient of 35° or higher was maintained the variation of either set of values from the mean was about 2 per cent. Below room temperature thedirection of heat flow was always from *A* to *B*. Extremely low temperature data could only be obtained with small gradients of the order of 4 to 6 degrees. It is therefore to be expected that these values would be low and that the per cent. deviation would be greater than athigher temperatures where larger gradients could be maintained.

drop vertically until it reached the line for the second state projected back. To test this point the specimen was held at a mean temperature of + 156° with a gradient of 12° for four hours. Absolutely no change in the thermo-electric power or resistance occurred throughout that time. The temperature was then raised to + 176° and held again for four hours. Again the thermo-electric power and resistance remained absolutely constant. A run was made very slowly through the entire transition region holding the temperature at each point constant for about three quarters of an hour. The points exactly checked the more rapid runs. The specimen was then cooled rapidly from 500° to points in the transition region with the idea of determining if the second state could be carried below 450° without the transition setting in. The rapid cooling curve exactly duplicated the slow heating one. The curves therefore appear to represent equilibrium conditions with a certain percentage of the second modification in solution in the first.

Up to 300° C. the thermo-electric power is positive with reference to platinum. It becomes zero at 300° and is negative above that temperature. The positive sign means that current flows across the hot junction from platinum to germanium or that in the external circuit the direction of flow is from germanium to platinum.

## THE RESISTANCE LINE.

From liquid-air temperature to + 100° C. the resistance of germanium follows a definite exponential law of the type $R = Ae^{[(Q/kT)+aT]}$, requiring a minimum at − 116° C. and a change in the temperature coefficient at that point from negative to positive. Above 600° the law is again found to hold but with different constants. In the intermediate region the law is entirely obscured by the transformation. Resistance minima were found at − 116° C. and + 645° C. The law is the same as that found by the writer to hold for iron oxide ($Fe_2O_3$) and was tested by a graphical method previously applied to that material.[1] This law is obtained by substituting for the empirical expression $R = R_0(1 + \alpha t + \beta t^2)$ the exponential form $R = R_0 e^{aT}$, which holds equally well, and combining with this the expression $N = N_0 e^{Q/kT}$ where $N$ means the number of electrons taking part in electrical conduction. This latter expression was originally suggested by Königsberger[2] as representing the way the number of free electrons increases with temperature. Replacing $R_0$, by $Ae^{Q/kT}$ we have the law indicated above. $A$, $Q$, $k$ and $a$ are constant. Königsberger tested the law for several of the so-called non-metallic con-

[1] Bidwell, PHYS. REV., N. S., VIII., No. 1, 1916.

[2] Königsberger and Schilling, Ann. d. Phys., 32, 179, 1910.

ductors in the form $R = A(1 + \alpha t + \beta t^2)e^{Q/kT}$ by solving for the constants from known data and then checking computed values against observed ones. As has been shown the law in the modified form may be tested graphically by differentiating and writing the expression in the form

$$\frac{1}{R}\frac{dR}{dT} = \left(-\frac{Q}{k}\right)\frac{1}{T^2} + a.$$

$dR/dT$ is the slope of the resistance line and may be measured. If the law is true we should get a straight line by plotting values of $(1/R\ dR/dT)$ as ordinates against values of $(1/T^2)$ as abscissa. The plot of this equation is shown, Fig. 3. It is apparent from this line that the law expresses

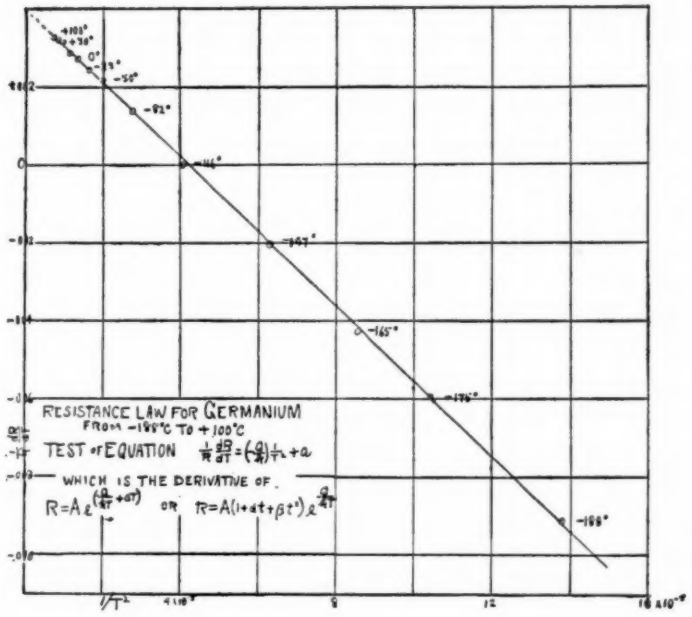


Fig. 3.

accurately the relation between resistance and temperature which is here followed.

### *Periodic Relations among the Elements with Reference to Temperature Variation of Resistance.*

A reference to the Periodic Table and Group IV. to which germanium belongs is very instructive. Carbon, the first element in this group, appears to follow a similar law with a minimum at some very high temperature. Silicon, titanium and zirconium have been studied by

Königsberger[3] and found to follow the law. Silicon has a negative temperature coefficient with a minimum obscured by transformations but apparently not as high as that of carbon. Titanium shows a minimum at about + 100° C. Germanium now falls in line with a minimum at − 116° C. Zirconium and tin[1] show inflections at still lower temperatures indicating an approach to a minimum. It may be well to recall in this connection that the extremely high resistance elements which occur toward the right end of the Periodic Table have characteristically negative temperature coefficients, while the very good conductors which occur usually toward the left end have positive temperature coefficients of resistance.[2] The Group IV. elements which in respect to so many properties are the transitional elements, are in this sense also the transitional ones, for in this group the change from positive to negative temperature coefficient of resistance occurs at temperatures within reach and while the element is in the solid state. As the heavier elements are characteristically better conductors than the lighter ones the transition from positive to negative would be expected to occur for these farther to the right, or in the same group the transition from negative to positive coefficient would occur earlier, *i.e.*, at lower temperatures for the heavier elements. This is borne out by the behavior of the Group IV. elements as shown above. In Group V. a careful study will probably reveal similar behavior for phosphorus, arsenic, antimony and bismuth. In Group VI. only the very heaviest elements may be expected to still show a positive temperature coefficient. At low temperatures the coefficient is still positive for tellurium.[3] In Group III. only the lighter elements may be expected to still have a *negative* coefficient. Boron,[4] the lightest, shows a negative coefficient. The minimum for boron has not been reported but is indicated as occurring at a very high temperature. The minimum for aluminum may possibly be located at a very low temperature. It is possible that beryllium of Group II. may show the transition if studied through the low temperature ranges. This work is now being undertaken.

That a single law should cover the resistance changes for ger-

[1] Onnes and Holst, Leiden Com., 142 (*a*), 1914.

[2] The elements are usually classified in this respect as conductors of the first class (those with positive temperature coefficients) and conductors of the second class (those with negative coefficients). Electrolytes which characteristically have negative temperature coefficients are usually included in this classification. Electrolytic conduction, however, is an entirely different phenomenon, follows a different resistance law and shows the distinctive characteristic of polarization. Electrolytes are to be considered as forming a separate class with which we are not here concerned.

[3] Onnes, Leiden Com., 132 (*d*), 1912.

[4] Weintraub, Jour. Ind. Chem., Feb., 1913.

manium up to a temperature of + 100° is strengthened by the behavior of the thermo-electric line through this region. This curve indicates that there is nothing in the way of a molecular transformation occurring at − 116° where the resistance minimum is found. The thermo-electric power is extremely susceptible to molecular modifications and therefore indicates where the resistance law may be expected to hold and where it may be expected to be obscured by the occurrence of molecular changes.

Data on resistance and thermo-electric power for several other rare elements will be reported in a later paper.

CORNELL UNIVERSITY,
December, 1921.

# MAGNETOSTRICTION WITH SMALL MAGNETIZING FIELDS.

BY JOHN R. HOBBIE, JR.

SYNOPSIS.

*Piezo-electric Method of Measuring Extremely Small Magnetostriction Effects.*—In this method, suggested by Pupin, the wire to be studied is surrounded by a solenoid through which an alternating current of known strength and frequency is sent, and the vibrations set up in the wire are transmitted to a piezo-electric crystal and the resulting electric charge is amplified and measured. (1) For elongations down to $2 \times 10^{-9}$ the wire was hung directly from a *quartz crystal*. To measure the charge produced by a given magnetizing current, an electromotive force of the same frequency and adjusted by means of a Pupin wave balance to the proper phase, was fed to the amplifier through a vacuum tube in parallel with the one connected to the crystal, and the potential was varied until the note produced by the crystal was balanced out. The force corresponding to a given charge was determined with the aid of a condenser, one plate of which was suspended from the crystal. (2) By using the torsion of a *Rochelle salt* crystal, the sensitiveness was extended to $2 \times 10^{-11}$, and (3) by tuning both the crystal and the wire to resonance with the frequency used, a sensitiveness of $3 \times 10^{-12}$ was reached. The last two arrangements were calibrated in absolute units by comparison of the results with those obtained with quartz. The smallest change previously measured was about $10^{-8}$.

*Magnetostriction with Small Magnetizing Fields.*—An *iron* wire containing 0.1 per cent. C, and a wire of *electrolytic nickel* were studied. In each case the curve for magnetostriction as a function of the field is nearly linear, but slightly concave downward, and apparently passes through the origin. For fields of 1, 0.05 and 0.002 gauss, the ratio of magnetostriction to field strength is respectively 3, 2.4 and $4 \times 10^{-9}$ for iron, and 2, 1 and $3 \times 10^{-9}$ for nickel. The probable error is from 7 to 10 per cent. *The effect of increasing the tension* is to decrease the elongation of both metals. A rod of *bismuth* 8 cm. long was tested in a field of 12 gauss using the resonance method, but gave a negative result, indicating that the effect is at least 10,000 times less than for iron.

*Pupin Wave Balance for varying the Phase of an Alternating Electromotive Force* is described.

## HISTORICAL.

OBSERVATIONS on magnetostriction, that is, on the change in the length of a piece of iron when subjected to a magnetic field, were made by Joule[1] in 1847. In 1873 Mayer[2] made a series of careful measurements of the effect and obtained coefficients of elongation and contraction which ranged from $4.86 \times 10^{-7}$ to $4.78 \times 10^{-7}$.

A very thorough study of magnetostriction was made by Bidwell[3]

[1] J. P. Joule, "On the Effects of Magnetostriction upon the Dimensions of Iron and Steel Bars," Phil. Mag., XXX., 1847, pp. 76, 225.

[2] A. M. Mayer, "On the Magnetic Elongation of Rods of Iron and Steel," Phil. Mag., XLVI., 1873, p. 177.

[3] Shelford Bidwell, "On the Changes produced in the Length of Rods of Iron, Steel, and Nickel," Proc. Roy. Soc., Vol. 38, 1885, p. 265; Vol. 40, 1886, pp. 109, 257; "On the Changes

in investigations extending from 1885 to 1890. An optical lever was used to measure the change in length, and he was able to detect a change of $10^{-7}$ times the length of his specimen with accuracy. The iron was found to increase in length with increasing magnetization up to a certain critical value, at which the maximum elongation was reached. Beyond the critical value, the elongation diminished, and a large magnetizing field produced contraction. Nickel contracted at first, and continued to contract, even with magnetizing forces far greater than those which produced the maximum elongation in iron. Tension decreased the elongation in iron, and increased the contraction.

Nagaoka[1] in 1894 examined the hysteresis effects attending magnetostriction. He used an optical lever and a micrometer microscope, and was able to detect changes in length of about $10^{-7}$ centimeters.

In 1898 Stevens[2] measured the change in length by observing the shift produced in interference bands. The smallest change that he was able to detect was $4 \times 10^{-8}$ per unit length.

## General Method.

The attention of these investigators was devoted to a study of magnetostriction with large fields. Their methods did not permit its study with small fields. The method of the present investigation permits of its study with very small fields, and was invented by Professor Pupin, of Columbia University.

An alternating current of approximately five hundred cycles was applied to a helix surrounding the specimen, a stretched iron wire. Since the elongation did not depend upon the direction of the magnetizing field, the wire vibrated with a frequency twice that of the current. A piezo-electric crystal, either quartz or Rochelle salt, was attached to one end of the vibrating wire, and an alternating electromotive force was developed on the tin foil coatings of the crystal by varying the tension of the wire. This electromotive force was increased by a three-stage amplifier to such an extent that it produced a note in a telephone receiver, and thus indicated the presence of vibrations in the wire. The amplitude of these vibrations was determined by balancing out the note with a known electromotive force of opposite phase to that developed on

produced by Magnetization in the Dimensions of Rings and Rods of Iron and of some other Metals," Proc. Roy. Soc., Vol. 43, 1888, p. 406; Phil. Trans., Vol. 179, 1888, p. 205; "On the Effect of Tension upon Magnetic Changes of Length in Wires of Iron, Nickel, and Cobalt," Proc. Roy. Soc., Vol. 47, 1890, p. 469.

[1] H. Nagaoka, "Hysteresis attending the Change of Length by Magnetostriction in Nickel and Iron," Phil. Mag., XXXVII., 1894, p. 131.

[2] J. S. Stevens, "An Application of Interference Methods to a Study of the Changes Produced in Metals by Magnetization," Phys. Rev., Vol. 7, 1898, p. 19.

the crystal. As the crystal had been calibrated by determining the potentials required to balance tensions of various amplitudes, the amplitude of the vibrations in the wire could be calculated.

With the larger magnetizing fields a quartz crystal was used. The specimen hung from the crystal, as shown in Fig. 1, and the helix through which the magnetizing current passed was wound directly on the wire. Approximately half the length of the wire was wound in this manner.

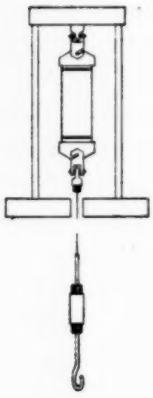

Fig. 1.

Method of suspending quartz crystal and wire.

If it is assumed that the rigidity of the crystal and its supports was large compared to that of the wire, and that the mass suspended from the wire was large compared to the mass of the wire, we can write, owing to the large frequency and large suspended mass used,

$$K = -Fl/l'sY, \tag{1}$$

where $K$ is the amplitude of elongation per unit length due to a given magnetizing field, $F$ the amplitude of the variation in tension due to the elongation, $l$ the total length of the wire, $l'$ the length of the magnetized portion, $s$ the cross section, and $Y$ Young's modulus for the wire.

That which was measured directly was not $F$ but the virtual electromotive force, $E$, developed on the crystal. A determination of the relation between $E$ and $F$ was necessary.

To effect this, one plate of a parallel plate condenser hung from the quartz crystal, and the other plate was placed just below it on a board which could be raised or lowered by levelling screws. Suppose now that a known electromotive force of the same frequency as that applied to the helix is applied to the condenser. The force of attraction of the lower plate upon the upper one is easily calculated and the electromotive force developed on the crystal found in terms of the mechanical force acting on it.

The attractive force is given by the equation,

$$F_0 = AV^2(10^{-4})/72\pi d^2, \tag{2}$$

where $F_0$ is the virtual attractive force between the condenser plates, $A$ the area of the plates, $V$ the virtual electromotive force applied to the condenser, and $d$ the distance between the plates of the condenser.

If we write, for the relation between the tension produced on the crystal and the electromotive force developed by it, $F_0 = Ez$, we have, since the attractive force $F_0$ is related to the amplitude $F$ of the tension

producing a virtual electromotive force $E$ on the crystal by the equation,

$$F = \sqrt{2}\, F_0,$$
$$F = \sqrt{2}\, Ez, \quad \text{or} \quad K = -\sqrt{2}\, Ezl/l'sY = \sqrt{2}\, EzD. \qquad (3)$$

The balancing electromotive force, of the same frequency as that developed by the crystal, was obtained by applying the magnetizing current to the grid of a vacuum tube. The arrangement is shown in Fig. 2. The magnetizing current, obtained from an alternating current machine giving a pure sine wave of 535 cycles, was applied to the grid of the tube $T_1$. A resistance between the grid of this tube and ground maintained the grid at a negative potential with respect to the filament, and the resulting distortion of the plate current gave rise to a series of overtones. The fundamental and all overtones except the first were short-circuited by a circuit $TC$ 1, tuned to resonance at 1,070 cycles. The current of double frequency thus obtained was increased by a power tube $T_2$.

An electrostatic voltmeter $V$ was used to measure the voltage, and a potentiometer $P_1$ to take off the amount needed for balancing.

The phase of the balancing electromotive force was regulated so as to be opposite to that produced by the crystal by a wave balance, $WB$, developed by Professor Pupin. It consists of a number of coils in series, with a condenser between each pair of coils and ground. These coils, which constitute the primary, are wound on a single tube in such a way that a secondary coil fitting over the tube can be moved along it. When an alternating electromotive force is applied to the first coil it is transmitted along the coils with a varying phase and a continuously diminishing amplitude. The attenuation has such a value that no stationary wave effects due to reflection at the end of the wave balance are appreciable. An electromotive force is induced in the secondary, the phase and amplitude of which depend upon its position on the primary coil.

In the particular wave balance used, the size and number of coils and condensers were such that there was a change of phase of about two hundred degrees from one end of the primary coil to the other. Thus, with the aid of a reversing switch $S_2$ in the secondary circuit, an electromotive force of any desired phase could be obtained for balancing.

To balance the electromotive force from the crystal and from the wave balance two repeating tubes, $T_3$ and $T_4$, Fig. 2, were connected in parallel as shown. The amplification ratio, $A$, of the two tubes was determined by sending to the grid of $T_4$, through a potentiometer $P_2$–$P_3$, and a two-way switch $S_3$, the same current that was supplied to thew ave-balance and its tube.

A test of the constancy of this ratio for various settings of potentiometer 3 was made, and the average variation from the mean found to be only about one per cent.

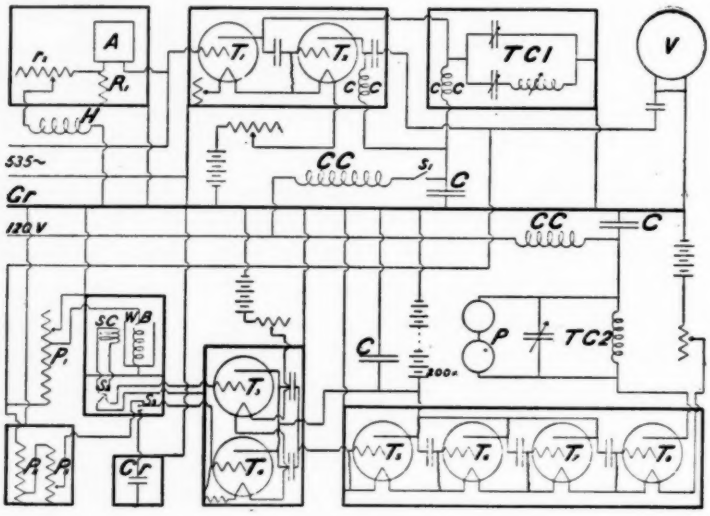


Fig. 2.
Diagram of electrical apparatus.

Equation (3) can now be written in the form

$$K = \sqrt{2}\, DzAP_1WV, \tag{4}$$

where $P_1$ is the ratio of potentiometer 1, $W$ the ratio of the wave balance, and $V$ the voltage applied to potentiometer 1.

The combined current from the two repeating tubes passed through a three-stage amplifier, made up of tubes $T_5$, $T_6$, $T_7$, the plates of which were fed from a two hundred volt dry battery. $T_8$ was a power tube used to supply the current to actuate the telephones $P$. A circuit $TC$ 2 was adjusted to resonance for the frequency of the note which was to be heard in the telephones.

Complete electrical shielding was found necessary to prevent the amplifier from picking up stray oscillations which interfered with the balancing. This shielding is indicated in the figure by heavy lines. All parts of the circuit were grounded radially to the heavy ground wire, $Gr$.

The magnetizing helix surrounding the iron wire is shown at $H$. It was fed from the alternator through an ammeter $A$ and a variable resistance $r_2$, which regulated the current flowing in the helix, in shunt with $R_1$. The amplitude of the magnetizing force is given by

$$H = 4\pi nI\sqrt{2}/10, \tag{5}$$

where $n$ is the number of turns of wire per centimeter in the helix. The factor $\sqrt{2}$ is introduced since $I$, as determined from the ammeter reading, is the virtual current.

The coils $CC$ were choke coils of sufficient impedance to prevent commutation from the one hundred and twenty volt machine entering different parts of the circuit, and to prevent oscillations set up at one point from reaching a point where they were not desired. The condensers $C$ served the same purpose by furnishing a ground for any current which might get by the choke coils.

## Use of Rochelle Salt.

Below one gauss, the results with quartz were not dependable, so Rochelle salt was used for the lower fields. The absolute value of $K$ could not be calculated with the Rochelle salt, but the shape of the curve could be determined, and matched up with the curve obtained by the quartz for the same region, thus getting the value of $K$ indirectly.

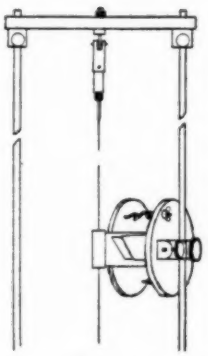

Fig. 3.

Method of supporting Rochelle salt crystal and wire.

The Rochelle salt crystal used was obtained through the kindness of Dr. A. M. Nicolson of the Western Electric Company. The mounting was the same as he had used in a phonograph transmitter,[1] and the method of attaching it to the wire is shown in Fig. 3. The iron wire hung from a brass block, the vibration of which was communicated to the crystal. The block was supported by a brass wire. In this way the weights suspended from the iron wire were supported by the brass wire and produced no strain on the crystal, but the elasticity of the brass wire permitted the vibrations due to the magnetostriction to be transmitted to the crystal. The vibration produced in the crystal was a torsional one, to which the crystal was most sensitive.

## Resonance Method.

To increase the sensitiveness of the method still more, Professor Pupin suggested using a wire and a crystal resonant to the frequency of the impressed vibrations.

A Rochelle salt crystal which, with its mounting, had a natural frequency between 1,050 and 1,100 vibrations per second was used in connection with a wire which had a length of one wave-length for longi-

[1] A. McL. Nicolson, "The Piezo-Electric Effect in the Composite Rochelle Salt Crystal," Proc. Am. I. E. E., Vol. 38, p. 1315, Nov., 1919.

tudinal vibrations of this frequency. The resonant crystal was furnished by Dr. Nicolson.

This wire was stretched in a horizontal position and held tightly by passing over a pulley and hanging weights from the end. Connection between the wire and the crystal was made in such a manner that the crystal could be moved back and forth from the end of the wire until a point was found where the note was of maximum intensity.

The alternator previously used was replaced by an oscillator, so that the frequency could be varied over a small range. To tune the circuit, the length of the wire was changed by moving a stop at its far end until a note of maximum intensity was produced when the oscillator was adjusted to a frequency corresponding to the length of the wire. This was taken to be the resonant frequency of the crystal.

Calculation of the absolute value of $K$ could not be made directly, so the shape of the curve was obtained, and the ordinates multiplied by the proper constant to make them fit the previous curves.

## METHOD OF EXPERIMENTATION.

For any run with the quartz crystal the switch $S_3$, Fig. 2, was thrown so as to connect the grid of $T_4$ with the potentiometer 3, and the note produced by the current from potentiometers 2 and 3 was balanced out by adjusting potentiometer 1 and the wave balance. This balance was made by setting the potentiometer and wave balance alternately for minimum sound in the telephone, until no sound was heard.

After measuring the amplification ratio, the crystal was connected to the grid of $T_4$, and a run was made by balancing out the note produced by the crystal under varying conditions.

## RESULTS WITH QUARTZ.

Runs with the quartz crystal were made with an iron wire containing about one tenth of one per cent. of carbon, and with a wire of electrolytic nickel. Both the iron and the nickel wires were stretched to remove kinks, then annealed by heating to a red heat.

The smallest weights used were found to be necessary to keep the wire stretched; the largest weights were about as much as could be used without producing a permanent stretch in the wire. The mean results of several runs under different conditions are shown in Figs. 4, 5, and 6.

The general character of the effect agrees with that which Bidwell obtained for small fields. The fact that a contraction is obtained in the case of nickel does not appear from the present method, which measures only the magnitude of the change, but does not indicate whether it is an elongation or a contraction.

The precision of the results shown in these curves is from seven to ten per cent.

The results with quartz correspond to those of Bidwell. This, together with the fact that a brass wire in place of the iron gave no sound, shows

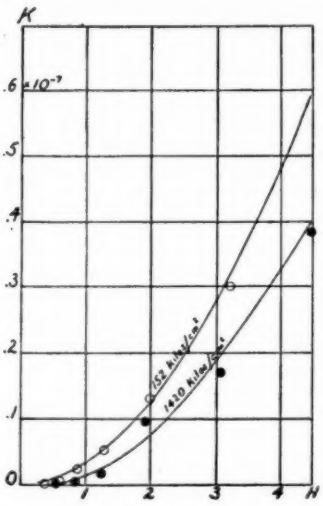


Fig. 4.

Amplitude of elongation per unit length vs. amplitude of magnetizing field (gauss). Low and high tensions. Quartz crystal. Iron wire.

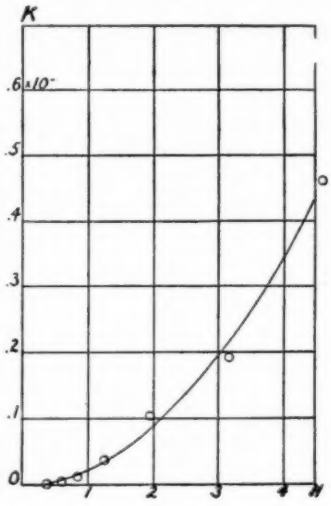


Fig. 5.

Amplitude of elongation per unit length vs. amplitude of magnetizing field (gauss). Low tension. Quartz crystal. Nickel wire.

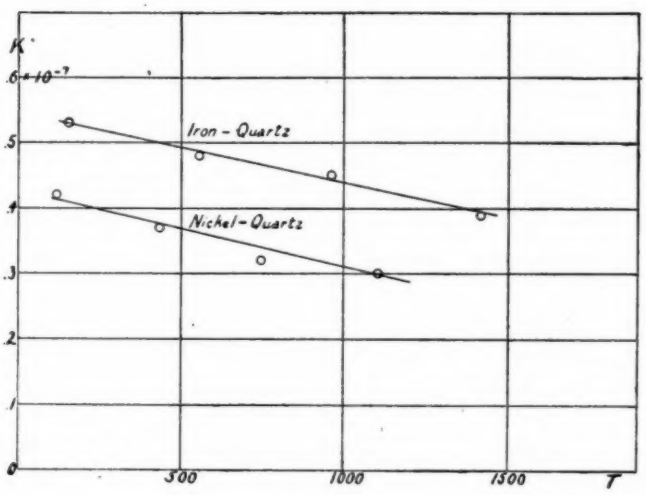


Fig. 6.

Amplitude of elongation per unit length vs. tension in wire (kgms./cm.²). Quartz crystal. Iron and Nickel Wires.

that the effect is due to magnetostriction, rather than to any direct magnetic effect of the helix.

## RESULTS WITH ROCHELLE SALT.

The results with quartz were most dependable above one gauss. The Rochelle salt gave curves that checked with those of quartz if the magnitude of the field was not greater than two gauss. For this reason

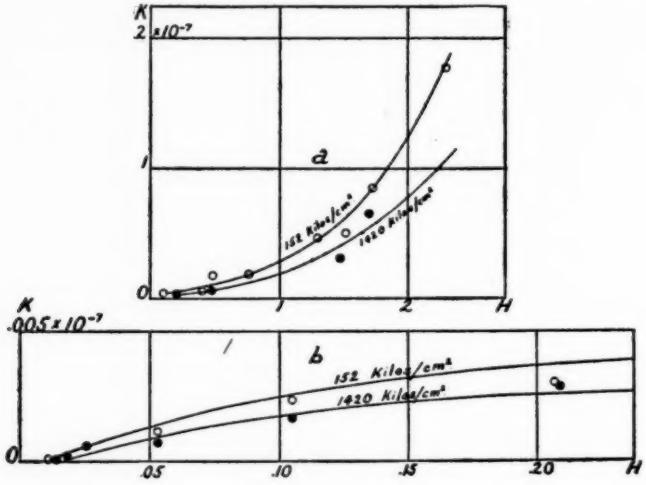


Fig. 7.

**Amplitude of elongation per unit length vs. amplitude of magnetizing field (gauss). Low and high tensions. Rochelle salt crystal. Iron wire.**

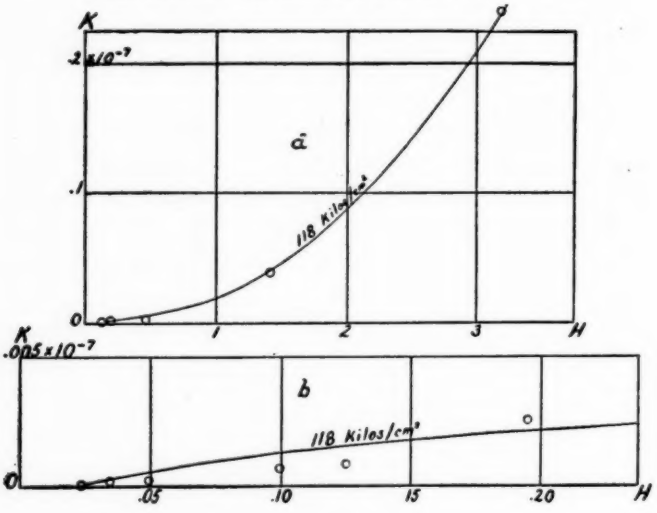


Fig. 8.

**Amplitude of elongation per unit length vs. amplitude of magnetizing field (gauss). Low tension. Rochelle salt crystal. Nickel wire.**

the multiplying factor applied to the Rochelle salt values was such as to make them fit the quartz curve most closely between one and two gauss.

The results are plotted in Figs. 7 *a* and *b*, and 8 *a* and *b*. The larger scales show the lower portions of the curves. A blank run with a brass wire gave no effect.

With the resonant wire and crystal the greatest effect was obtained when the tension in the wire was greatest, so the runs were made with the maximum tension, 1420 kilos per square centimeter, previously used. The results with the iron wire are plotted in Fig. 9 *a*, *b*, *c*, on successively

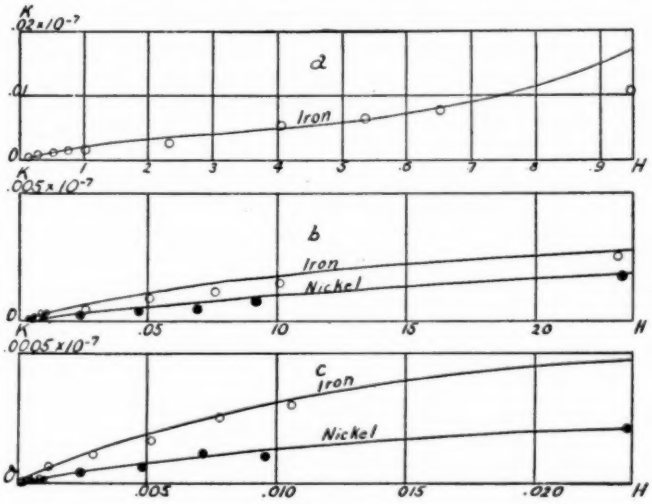


Fig. 9.

Amplitude of elongation per unit length vs. amplitude of magnetizing field (gauss). Resonant wire and crystal. Iron and Nickel Wires.

larger scales. Comparison of Figs. 7*a* and 9*a* shows that the resonant curve fits the previous one for values of $H$ less than 0.6 gauss. Above this value the resonant curve is less, doubtless due to excessive damping in the case of the vibrations of greater amplitude. The curves shown in Fig. 9 *b* and *c* are more dependable than those in Fig. 7*b* for the lower portion of the curve.

Runs were made with the nickel wire in the same manner as with the iron, except that a tension of 747 kilos per square centimeter was used. The results are shown in Fig. 9 *b* and *c*. Since no run with the quartz crystal and nickel wire was made at this tension, the curves for nickel in Fig. 9 *b* and *c* can only be regarded as a rough approximation to the absolute value. Their shape, however, can be depended on.

By means of the resonant method the curve has been extended to 0.002 of a gauss in the case of iron, and to 0.005 of a gauss in the case of

nickel. At these values the effect could just be detected. A brass wire substituted for the iron or nickel produced no effect.

In each case the shape of the curve was the same; that is, nearly linear but slightly concave downward in its lower portion, apparently passing through the origin.

## EXPERIMENTS WITH BISMUTH.

In the account of Bidwell's work[1] he tells of detecting magnetostriction in bismuth. The effect was small but measurable. Later Wills[2] undertook to measure the effect. Using specially prepared very pure bismuth and an apparatus which would have detected a change of $10^{-8}$ times the length of the specimen, one centimeter, he was unable to observe any effect with a field as high as 3,200 gauss.

If Bidwell's results were correct, a field of seven gauss should give an elongation great enough to come within the limits of the resonant method, about $3 \times 10^{-12}$. A rod of bismuth about eight centimeters long and one half a centimeter in diameter was wound with a helix to within about one centimeter of each end, and attached to a brass wire of the resonant length.

The power of the amplifier was increased, and a field of twelve gauss applied to the bismuth, but without producing any effect. It would seem, then, that magnetostriction is lacking in bismuth, at least in fields of twelve gauss.

The writer wishes to express his obligations to Professors Pupin and Wills for frequent suggestions made during the development of the method and the progress of the investigation, and to the Western Electric Company and Dr. Nicolson for their kindness in furnishing the crystals of Rochelle salt, and in giving suggestions as to their use.

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COLUMBIA UNIVERSITY,
August, 1921.

[1] Shelford Bidwell, "On the Changes Produced by Magnetization in the Dimensions of Rings and Rods of Iron and of Some other Metals," Phil. Trans., Vol. 179, 1888, p. 205.

[2] A. P. Wills, "On Magnetostriction in Bismuth," PHYS. REV., Vol. 15, 1902, p. 1.

# A NOTE ON THE PRESSURE OF RADIATION ON TRANSPARENT DIELECTRICS.

BY SATYENDRA RAY.

SYNOPSIS.

*Suggested Explanation of Photophoresis*, that is the attraction or repulsion of microscopic particles by light as observed by Ehrenhaft and others. It has previously been shown that there are electric and magnetic forces acting on an illuminated transparent body in the direction of propagation of the light if the ether has an electric density (*Pe*) and a magnetic density (*Pm*) other than zero. When one dielectric is immersed in another, the difference between these radiation forces per unit volume acting on the two media, would give rise to a relative motion which may be either in the direction of the light or in the opposite direction.

*A Quantum Relation in Maxwell's Electromagnetic Theory* is obtained if we equate the radiation pressure per unit area in terms of *Pe* and *Pm* to the pressure derived from the stresses assumed by Maxwell to exist in electric and magnetic tubes of force, namely, the ratio of the amplitude to the wave-length of light is a constant.

THE phenomenon of "negative photophoresis" discovered by Ehrenhaft requires a reëxamination of our notion of radiation pressure. The most serious difficulty in the way of a radiometric interpretation of the phenomenon as given by Westphal and Gerlach, Rubinowicz, Laski and Zerner, etc., is the doubt it throws on the experiments of Lebedew, and Nichols and Hull as having established this radiation pressure. Millikan points out how the droplet suspended in his condenser by the proper electrical field forms an electrical balance that "will weigh accurately and easily to one ten-billionth part of a milligram." Ehrenhaft's condenser using (1) much smaller particles and (2) a microscope in place of a telescope for observations, is quite a thousand times more sensitive. Again, as Ehrenhaft points out (Ann. d. Phys., 56, p. 83) for spherical particles radiation pressure is proportional to the square of the radius while its mass is proportional to its cube so that the acceleration effect would be inversely proportional to the radius and becomes infinitely great for infinitely small values of $r$. If then under such highly favorable conditions, theoretical as well as experimental, we find the "photophoretic force" almost as often as not [1] negative in character and if to

[1] An interesting relation between the photophoretic character of an element and its position in the periodic table is given by Mattauch in the following words, "Wie F. Ehrenhaft in einem Vortrage über die Photophorese in der chem.-phys. Ges. in Wien (März, 1919) erwähnte, erweisen sich, soweit die Materialien bisher von ihm und seinen Schülern untersucht sind, Na, K, Cu, Ag, Au, ferner Mg, Zn, Cd und Hg, also die Elemente der Kolonnen I und II des periodischen Systems als lichtpositiv. Lichtnegativ dagegen sind S, P, Sn, Pb und Te, also die Elemente der Kolonnen III und IV und ebenso der Kolonnen V bis VII. Die den letz-

explain the negative sign we are thrown back upon a radiometric explanation, all experiments hitherto done to experimentally establish radiation pressure are naturally discredited.

In this connection attention is invited to a paper by Michaud, who, in order to explain negative photophoresis, showed from thermodynamic considerations the possibility of light pull instead of light pressure for *transparent* substances.[1]

In the radiometric interpretation of negative photophoresis it is assumed that it is impossible to explain it on the electromagnetic theory of light.[2] It would be interesting to examine the *steady* forces in the beam of light mentioned in the note on the plane wave[3] for an explanation of negative photophoresis.

The constant intensities in the direction of propagation of a plane wave lead us to a simple expression for the pressure of radiation on transparent bodies. The constant intensities $2\rho_e\Lambda/K$ and $2\rho_m\Lambda/\mu$ give us, by definition, forces acting per unit charge in a direction parallel to that of propagation. The forces per unit volume would be $2\rho_e^2\Lambda/K$ and $2\rho_m^2\Lambda/\mu$ respectively. The mechanical force per unit volume would be the sum of these two forces

$$F = \left(\frac{2\rho_e^2\Lambda}{K} + \frac{2\rho_m^2\Lambda}{\mu}\right).$$

The pressure in the usual form of force per unit area may be derived from the expression

$$F = \tfrac{1}{2}R \cdot N,$$

where

$$R = \frac{4\pi}{K} \cdot N.$$

Substituting for $R$ the value $2\rho_e\Lambda/K$ we have, therefore, due to the electric force,

$$F_1 = \frac{\rho_e^2\Lambda^2}{2\pi K}.$$

Similarly, due to the magnetic force,

$$F_2 = \frac{\rho_m^2\Lambda^2}{2\pi\mu}.$$

teren Kolonnen angehörenden Elemente As, Se, Sb, Te und J, die in verschiedenen allotropen Modifikationen auftreten, haben aber, wie dortselbst auseinandergesetzt wurde, noch die besondere Eigenschaft dass bei ihrer Verdampfung sowohl lichtpositive als auch lichtnegative Probekörper entstehen." Neue Versuche zur Photophorese, Sitzungsber. d. Wien. Akad. d. Wiss., 129 (IIa), 1920.

[1] C. R., Vol. 168, Nr. 15, 14 April, 1919.

[2] Zerner and Laski in Zeit. f. Physik., March 4, 1920, p. 226.

[3] PHYS. REV., Nov., 1921.

And the resultant force,

$$F = \frac{\Lambda^2}{2\pi}\left(\frac{\rho_e^2}{K} + \frac{\rho_m^2}{\mu}\right). \qquad (1)$$

We notice the expression on the right-hand side is of the dimensions of a pressure, and that it is, apparently, independent of the amplitude of vibration in the light disturbance. Maxwell's conception of stresses in the electric and magnetic tubes of force gives us another expression for the pressure, namely $KR^2/8\pi$. Obviously the two expressions are not independent of one another. They are either equal or bear a constant ratio to one another. We have

$$\frac{\rho_e^2\Lambda^2}{2\pi K} = \frac{c \cdot KR^2}{8\pi}$$

or

$$\frac{R^2}{\Lambda^2} = \frac{1 \cdot 4\rho_e^2}{c \quad K^2} = \text{constant.}$$

In words; the ratio between the amplitude and wave-length of light is constant. This interesting relation leads us to a quantum relation in Maxwell's electromagnetic theory and makes the law of equipartition of energy satisfied in the light-wave through ether.

Equation (1) gives us a steady pressure instead of the average of a variable effect and is obtained directly from the fundamental equations. The magnitude of this constant force will depend upon the dielectric. In the case of one dielectric being immersed in another the difference in magnitude of force per unit volume will cause a relative motion parallel to the direction of propagation. The sense of motion, however, can as easily be towards the source of light as away from it. A particle immersed in a fluid gives us a gravitational analogue. The earth's pull exerts a downward force on the particle immersed as well as on each element of the fluid. Whether the particle would rise or sink depends upon whether its gravitational density is smaller or greater than that of the fluid. In this analogy "negative photophoresis" corresponds to buoyancy.

In connection with the "electric density" of dielectrics attention may be directed to an aspect of modern atomic theories. They are not neutral.[1] The necessary excess of charge gives us an electric density.

[1] Broughall, Phil. Mag., Vol. 41, p. 872.

University College, London,
December 16, 1921.

# THE ELECTRODELESS DISCHARGE IN CERTAIN VAPORS.

BY J. K. ROBERTSON.

SYNOPSIS.

*Appearance and Spectrum of Electrodeless Discharge in Various Vapors.*—The discharge was produced by electromagnetic induction, the bulbs containing the vapors being placed within a Tesla coil through which passed a high-frequency condenser discharge. The effect was found to *vary with vapor pressure*, controlled by the temperature, *and with electromotive force*, controlled by a spark gap. In general, for a certain range of pressure, an intense ring discharge was obtained which weakened to a faint luminosity for higher pressures. *Potassium* at temperatures of 250–300° C., gave a bright ring with a spectrum including seven or more members of each subordinate series. The bright yellow discharge in *sodium* above 300° C. showed the *D*-lines, four members of the diffuse series and three members of the sharp series. With *lithium* up to 500° C. only a feeble discharge due to impurities was obtained. In the case of *mercury*, the work of Kowalski was confirmed and extended. A dazzling white ring discharge appeared from 70 to 110° C. or higher depending on the spark gap; then became fainter, while a greenish glow whose spectrum showed a few lines superposed on a continuous band extending from the violet to the yellow, appeared for 110 to 115° C., *irrespective of the spark gap*. It is suggested that the glow may be associated with polyatomic molecules formed at the higher vapor pressures. In the case of *iodine*, the only diatomic vapor studied, at temperatures from − 5° to 5° C. a pale yellow ring showing a band spectrum changed to a green, pink-bordered ring with a line spectrum when the spark gap was increased; the higher the pressure, the greater the spark length necessary to excite the line spectrum. The change probably accompanies dissociation of the molecules into atoms.

*Electrodeless Discharge as a Source of Sharp Lines* should be of value in measuring wave-lengths and in analyzing, with an instrument of high dispersion, lines with components due to isotopes.

ALTHOUGH the subject of investigation by Sir J. J. Thomson as long ago as 1892, the electrodeless discharge has been utilized but little by spectroscopists. Some time ago it occurred to the writer that it might be worth while to try to obtain this type of discharge in the case of the more easily vaporized metals. Because of the comparatively simple conditions of discharge, combined with the absence of electrodes and the ease with which ordinary impurities can be avoided, it was thought that much valuable information might be gained from such a spectroscopic study. Circumstances have not made possible as yet an exhaustive investigation, but enough has been done to show that this type of discharge provides a most useful source for the study not only of the vacuum arc spectrum of such metals as sodium and potassium, but also, as in the case of the diatomic vapor of iodine, of the change in the spectrum brought about by dissociation. Since the investigation was

undertaken, it has been noted that McLennan[1] made use of this type of discharge in his work on the spectral series of mercury, while Kowalski[2] examined the change in the appearance of the discharge in the same vapor with changing temperature. Hagenbach and Frey,[3] moreover, have made a preliminary report of a spectroscopic study of the discharge in many gases and vapors. It will be seen below, however, that these writers, in the case of sodium and of iodine, failed to obtain the proper discharge. Quite recently Dunoyer[4] has published a report on the spectrum of cæsium, obtained also from the discharge excited by electromagnetic induction.

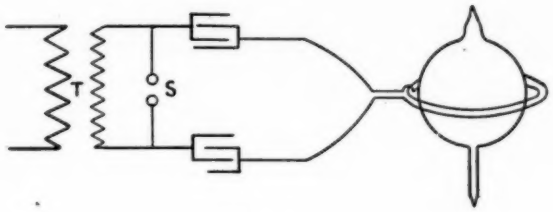



Fig. 1.

The experimental arrangement differed little from that first used by Sir J. J. Thomson. A bulb, some 12 cm. in diameter was suspended inside a coil of six co-planar turns of stout copper wire through which passed the high-frequency oscillatory discharge of two Leyden jars connected as shown in the diagram (capacity of each $5\text{–}7 \times 10^2$ absolute electrostatic units). A clearance of some two to four millimeters existed between the outside of the bulb and the innermost turn of the coil. The jars were charged in some cases by an induction coil but subsequently by means of a small interrupterless x-ray transformer $T$, while the spark gap $S$ enabled one to control the intensity of the exciting field inside the bulb. It may be noted here that Bergen Davis[5] has shown that the mean value of the electrical intensity inside the bulb is directly proportional to the potential at the spark gap.

By means of a Langmuir condensation pump with auxiliary, the bulbs of pyrex glass were exhausted to a pressure of the order of 0.0002 mm. Hg., the flame of a large Meker burner being played over each of them for an hour during exhaustion. The vapor of the element to be used was then distilled over from a side tube, and the bulb finally sealed off both from the side arm and from the pumps. In the case of sodium,

[1] J. C. McLennan, Proc. Roy. Soc., A, 87, p. 256.
[2] J. Kowalski, Phys. Zeit., XV., No. 5, p. 249.
[3] Hagenbach and Frey, Phys. Zeit., XVIII., p. 544, 1917.
[4] M. L. Dunoyer, Comptes Rendus, Tome 175, No. 6, p. 350.
[5] Bergen Davis, PHYS. REV., Vol. XX., p. 129, 1905.

before sealing off from the pumps, the metal was "chased" about the bulb a number of times to drive off as much as possible occluded hydrogen.[1] The bulb to be used was then suspended within the primary coil, which in all cases so far studied except iodine, was inside an electric oven. In this way vapor pressures corresponding to temperatures as high as 500° C. could be obtained if necessary.

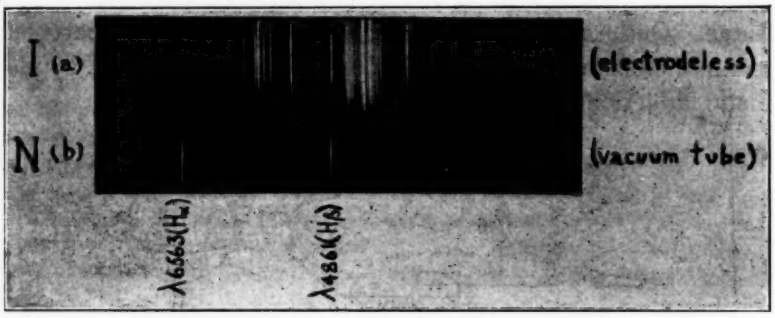



Fig. 2.

## IODINE.

To obtain the discharge in iodine a projecting stem of the bulb was immersed in a vessel containing melting ice. It was found that two distinct types of ring discharge could be obtained. With a spark gap of the order of 1 mm., the ring had a pale yellow appearance, probably the same color as the chamois yellow which Wood[2] describes. Examination with a spectroscope of small dispersion showed a continuous band extending from red to green, then a wide absorption band, followed by a second apparently continuous band in the blue-violet. As the spark gap was increased in length, the appearance of the ring changed abruptly to a pale green ring with an inner pink border, the latter extending to a slightly greater distance above the plane of the coil than the green luminescence. The spectrum of this second type of discharge showed numerous bright lines, with faint continuous background in the red region. Photograph *a* in the accompanying plate is a photograph of the spectrum of the "green" discharge, made with a Hilger constant deviation spectrograph. The abrupt change in the appearance of the discharge is doubtless the result of dissociation, the pink border probably corresponding to the lesser degree of dissociation one might expect in the weaker electric field nearer the center of the bulb. It was at first thought that the pink luminosity might be due to nitrogen present as an impurity,

[1] R. W. Wood, Researches in Physical Optics, Part II., p. 178, 1919.
[2] R. W. Wood, Researches in Physical Optics, Part II., p. 53, 1919.

Wood [1] having observed that color in insufficiently exhausted iodine vacuum tubes. It will be seen from the plate, however, that there is no trace of nitrogen as far as one can judge from *b*, the comparison spectrum

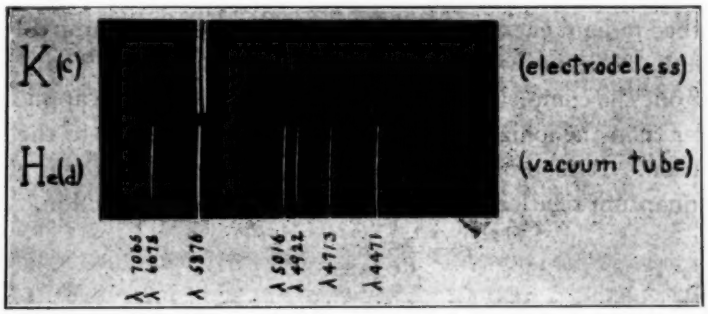



Fig. 3.

of a nitrogen vacuum tube (with hydrogen impurity). Observation with a small direct-vision spectroscope directed successively at the green and the pink portions of the ring showed that the lines in the pink were much feebler than in the green. This is what one would expect from a smaller degree of dissociation.

By varying the temperature of the bath in which the stem was immersed, it was shown that both types of ring discharge could be obtained at vapor pressures corresponding to temperatures lower than $-5°$ C. and higher than $+5°$ C. With increasing pressure, a longer gap was required to bring out the line discharge. This again is just what one would expect, because the higher the pressure, the shorter the free path of an electron or ion and so the greater the electric intensity necessary to give the electron the energy required to bring out the line spectrum.

As the pressure rises higher and higher, a stage is reached at which the discharge is accompanied by a general and comparatively feeble luminosity filling part or all of the bulb. It is not surprising that Hagenbach and Frey, who apparently worked with iodine only at room temperature, found the discharge in this case not brilliant.[2]

By slowly changing the spark gap, an attempt was made to see which line, if any, first became visible during the transition from the band to the line spectrum. A line approximately λ 4860 seemed to flash in first, although others followed so quickly that it was difficult to determine this conclusively. In this connection it is interesting to note that, if we apply the quantum relation, $eV = h\nu$, λ 4860 corresponds to a radiating poten-

[1] Researches in Physical Optics, Part II., p. 53, 1919.

[2] "Doch bildet sich die Ringentladung . . . nicht schön aus."—Hagenbach and Frey, loc. cit.

tial of 2.54 volts, while the value obtained for the resonance potential of iodine by direct experiment by Mohler and Foote[1] is 2.34 ± .2 volts. Moreover, Smyth and Compton,[2] in their work on the ionization of fluorescing iodine vapor, obtained 2.6 volts as a rough value for the quantum of absorbed radiant energy. This agreement, however, is probably purely accidental. Working with hydrogen, Franck[3] has shown that, in order to bring out the complete line spectrum, a voltage must be applied which is greater than the ionizing potential by an amount equal to the work of dissociation. It is probable, therefore, that in all diatomic gases the simple quantum relation cannot be applied without correction.

## POTASSIUM.

At temperatures ranging from 250° to 300° C. no difficulty was experienced in obtaining a bright ring discharge in the case of potassium. The ring which is not so sharply defined as in the case of iodine, consists of a pale green portion, with an outer border of orange yellow. If the electrical intensity is great enough, a distinctly violet region is seen next the bulb. The spectrum shows the ordinary arc lines, as will be seen from photograph *c* in Fig. 3 where *d* is a comparison spectrum of helium. It was not possible with the small dispersion of the spectroscope to make any exact measurements of wave-lengths. Lines of the first and second subordinate series as far as λ 4805 were easily identified. Then followed a group of two or three faint lines, then λ 4757 (rough setting), then a group of seven or eight or more, until λ 4643 was read. This last is no doubt the combination pair 4642.17 and 4641.58 recently observed by Datta.[4] Further in the violet region lines were observed at values approximately λ 4607, λ 4506, λ 4390 and λ 4314. It would seem, therefore, that with this source one may obtain if anything higher members of the subordinate series than those measured by Datta.[5]

The sodium D lines always came out strongly, and at times the red sodium lines at λ 6161 were faintly visible. A few unidentified lines were visible, for the most part very faintly, although one at λ 5007 and another at λ 4831 were at times moderately intense.

As his source of light Datta used a potassium vapor lamp, similar in construction to the sodium lamp devised by Lord Rayleigh,[6] but much more troublesome to operate than the sodium. With the electrodeless

[1] Mohler and Foote, PHYS. REV., Vol. XV., No. 4, p. 321, 1920.
[2] H. D. Smyth and K. T. Compton, PHYS. REV., Vol. XVI., p. 501, 1920.
[3] J. Franck, Phys. Zeit., XXII., p. 468, 1921.
[4] S. Datta, Proc. Roy. Soc., A, 99, April, 1921.
[5] S. Datta, loc. cit.
[6] R. J. Strutt, Proc. Roy. Soc., A, 96, p. 272, 1919.

arra ngement no difficulty whatever was experienced, and it was found that observations could be extended over a series of days. Indeed, a bulb which has been used on four or five different occasions, is only slightly discolored and may still be used for further observations.

Such a source, moreover, because of the low vapor pressure at which the luminous discharge occurs, should be suitable for a study of the structure of single lines. If potassium is a mixture of two isotopes, as recently shown by Aston, one might expect each line of a doublet to be made up of two components. It might be well worth while, therefore, to examine the structure of some of the potassium lines from the above source with a sufficiently high resolving power. Making use of the difference in wave-lengths obtained by Merton[1] for different specimens of lead (0.002 Å.u.–0.005 Å.u.) one might expect for potassium lines a separation of possible components approximately (0.002–0.005) × 207/40 or (0.01 Å.u.–0.025 Å.u.). The echelon at the disposal of the writer, however, has not a resolving power sufficiently high to detect a difference of that order.

## Sodium.

In the case of sodium at temperatures above 300° C. a brilliant yellow discharge filling almost the whole bulb was obtained. In addition to the D lines, the first four doublets of the diffuse series were identified, as well as the first three of the sharp series. The Balmer lines of hydrogen, the most likely impurity, were not visible. Hagenbach and Frey[2] observed only the D lines in the immediate neighborhood of a piece of the metal placed in the bulb, although they obtained a ring discharge showing mercury, nitrogen and carbon dioxide. Apparently their bulb was not exhausted thoroughly, nor was the sodium sufficiently vaporized.

With sodium an induction coil was used for charging the Leyden jars. With excitation similar to that used in the case of potassium and iodine, and at a temperature considerably above 300° C., it is highly probable that more and stronger lines would be brought out. As a matter of fact, evidence has been obtained of a more brilliant discharge in the case of a bulb excited in this way, but unfortunately because of a "short" which developed between the primary coil and the oven no observations were possible.

## Lithium.

By courtesy of the Metallurgical Department of Queen's University, a small quantity of lithium of unknown purity was obtained, and a bulb prepared. By using an iron capsule in the side tube a small quantity of

[1] Merton, Proc. Roy. Soc., A, 679, p. 388, 1920.

[2] Hagenbach and Frey, loc. cit.

metal was vaporized and deposited in the bulb, but although the oven was heated as high as 500° C., nothing but a feeble discharge due to impurities was obtained.

## MERCURY.

In common with Kowalski,[1] the writer observed with mercury, two distinct types of discharge—the first a dazzling white ring, the second a diffuse greenish glow which filled the whole bulb. The ring discharge showed numerous lines, the number increasing with increasing spark gap. One set of visual observations showed some 24 lines ranging from λ 6234 to λ 4339, twenty of which were identified with standard mercury lines belonging to the triplet, single line and combination series. Unidentified lines were observed at approximately λλ 6122, 5026, 4959. The spectrum of the greenish glow showed a continuous band upon which λ 5461 was superimposed, as well as λ 4959 and λ 4355, if the intensity was great enough. The continuous band seemed to end abruptly towards the red end at the two yellow lines.

The brilliant white discharge could be obtained at temperatures ranging from 70° to 110° C. or higher, the exact temperature at which it disappeared increasing with increasing spark gap. On the other hand, observations made with spark gap 1 mm., 2 mm., 4 mm. and 6 mm. in length indicated that the temperature at which the glow begins (110°–115°) is *independent* of the electrical intensity. The origin of the continuous spectrum, therefore, is probably closely connected with the density of the vapor. Very recently R. W. Wood [2] has made the statement that mercury vapor can be made to fluoresce only when freshly liberated from the fluid metal, and suggests that the formation of diatomic molecules is necessary for the phenomenon of fluorescence. That such a grouping of atoms is possible is evident from the work of Sir J. J. Thomson on Positive Rays, in the course of which he showed that even at the low pressures obtaining in his discharge tubes, it was possible to have clusters of four mercury atoms with a single positive charge. As such groupings would occur much more readily at vapor densities corresponding to temperatures over 100° C., it would seem that the "radiators" of the continuous spectrum are to be found in such clusters, an idea which has been previously suggested by more than one writer.[3]

With the temperature of the vapor approximately constant (at say 90° C.), observations were made at various spark lengths. It was found that below a minimum gap length (of the order of 0.5 mm.), the bright

[1] J. Kowalski, Physik. Zeit., 15, 225, 1914.

[2] R. W. Wood, Proc. Roy. Soc., A, 700, p. 362, 1921.

[3] C. D. Child, Science, Sept. 10, 1921. Horton, Phil. Mag., Vol. 22, p. 214, 1911.

white discharge gave place to a faint white luminosity whose intensity was greater in the plane of the coil, while above this length, the ring discharge appeared. At the critical stage, when the ring flashed in intermittently, the spectrum showed the five lines λλ 5791, 5770, 5461, 4916 and 4358. On increasing the gap, other lines quickly made their appearance.

In conclusion, the writer would like to emphasize the difference in the behavior of a diatomic vapor like iodine compared with that of monatomic vapors. It would seem that useful information concerning the spectra of diatomic gases, such as hydrogen, might be gained by a study of their electrodeless discharge, and it is planned to make such a study in the near future. The work planned includes an examination of the discharge in $CO_2$ and $N_2O$, to see if there is any similarity in the spectra of these two gases, whose molecules on the cubical atom theory of Lewis and Langmuir have almost identical electron structures.

Queen's University,
Kingston, Ont.,
October, 1921.

# PIEZO-ELECTRIC ACTIVITY OF ROCHELLE SALT UNDER VARIOUS CONDITIONS.

BY J. VALASEK.

SYNOPSIS.

*Electrical Properties of Rochelle Salt Crystal* are analogous to the magnetic properties of iron, the dielectric displacement $D$ and polarization $P$ varying with the electric field $E$ in the same general manner as $B$ and $I$ vary with $H$ for iron, and showing an *electric hysteresis* with loops distorted by an amount corresponding to the *permanent polarization* $P_0$, whose value is about 30 e.s.u./cm.$^2$ but varies for different crystals. The *dielectric constant* ($\kappa = dD/dE$) was measured *from* $-70°$ *to* $30°$ *C.* and found to be surprisingly large, increasing from about 50 at $-70°$ to a maximum of about 1,000 near 0°. The modulus of *piezo-electric activity for shearing stresses* ($\delta$) *varies with temperature,* $-70°$ *to* $40°$ *C.*, in a very similar manner, increasing from less than $10^{-6}$ at $-70°$ to a maximum of about $10^{-4}$ at 0°. The ratio $\delta/\kappa$ *varied with the electrode material*, being greater for tin foil than for mercury electrodes. The difference may be due to the alcohol used in shellacking the tin-foil electrodes on. There are other indications that $\delta$ and $\kappa$ are related. The *variation of* $\delta$ *with humidity* is such as can be accounted for by the decrease in the dielectric constant of the outer layer as a result of dehydration. The change of polarization produced by pressure as measured by the change in the hysteresis loop agrees with the value found directly from the piezo-electric response, as required by Lord Kelvin's theory. Also *fatigue effects on* $\delta$ produced by temporarily applied fields are traceable to fatigue in the polarization. The *electrical conductivity below* $45°$ is less than $5 \times 10^{-9}$ mhos/cm.$^3$ but *from* $43°$ *to* $57°$ increases rapidly to $5 \times 10^{-4}$.

*Optical Properties of Rochelle Salt as Calculated from the Natural Polarization.*—Assuming only one electron is displaced the *natural period* corresponds to a wavelength of 4.2 $\mu$ and the *specific rotation* for sodium light comes out 10°, the observed value being 22°.1.

RECENTLY[1] the writer described some experiments on the dielectric and piezo-electric properties of Rochelle salt, which were made for the purpose of correlating and explaining the effects observed chiefly by Cady and by Anderson. The plates used were cut with faces perpendicular to the ă axis and with edges at 45° with the $\bar{b}$ and c axes. The present paper is a continuation of the work, the variations in the electrical properties having been studied more extensively. The apparatus and method of observation have been already described in the paper referred to above. The more important results obtained at that time can be summarized as follows:

In the case of Rochelle salt the dielectric displacement $D$, electric intensity $E$, and polarization $P$ behave in a manner analogous to $B$, $H$, and $I$ in the case of magnetism. Rochelle salt shows an electric

[1] J. Valasek, PHYS. REV. (2), XVII, p. 475.

hysteresis in $P$ analogous to the magnetic hysteresis in the case of iron, the loops however being distorted by an amount corresponding to the permanent polarization of the crystal in the natural state. This point of view is very effective in accounting for many of the peculiarities observed.

In an electric field the piezo-electric activity has a maximum for a definite value of the field and decreases to a small value in both directions. The position of the maximum corresponds to the greatest rate of change of polarization with electric field in the case of the condenser experiments. In fact if force and electric field are equivalent in changing the piezo-electric polarization then the response for a given force in various applied fields must necessarily give curves of the same general nature as curves of $\partial P/\partial E$ or $\partial D/\partial E$ against $E$. It is permissible to interchange $D$ and $P$ in most cases because of the large dielectric constant of Rochelle salt.

RELATION BETWEEN POLARIZATION AND PIEZO-ELECTRIC ACTIVITY.

The activity of a piezo-electric crystal is intimately related to the natural polarization. According to Lord Kelvin this natural moment is masked by surface charges so that the crystal appears to be uncharged. This polarization or piezo-electric moment can be measured independently of the charges on the electrodes, through the distortion of the hysteresis loop. The center $A$ of the loop is found by a consideration of symmetry and may be assumed to represent the condition of no polarization. If the natural condition of polarization is assumed to be half way between the two branches of the loop at zero field then the value of the permanent polarization $P_0$ is proportional to $AB$, Fig. 1. There being

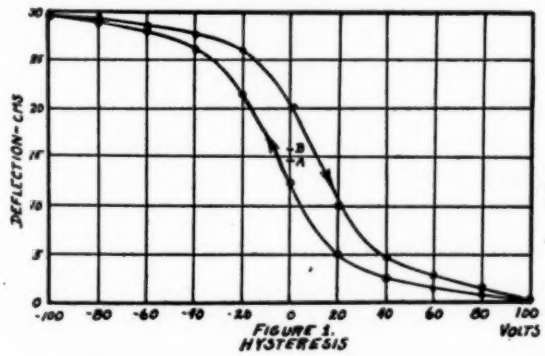



Fig. 1.

no field applied, the equation for the work done per unit charge carried through the condenser is:

$$4\pi\left(\frac{Q_0}{S} - P_0\right)l = 0,$$

so that

$$P_0 = \frac{Q_0}{S},$$

where $Q_0$ is the apparent average permanent charge at zero field given by $AB$ (Fig. 1) and where $S$ is the area of the plate. Calculation gives the value: 30 e.s.v./cm$^2$.

According to Lord Kelvin's theory an applied stress will change this polarization so as to create free charges on the electrodes. A force of 250 grams applied to the crystal should consequently shift the loop by an amount equivalent to the piezo-electric response for 250 grams. When this experiment was performed another, but more unsymmetrical loop, was obtained. The change in polarization by the loop method was 114 e.s.u./cm.$^2$ while the piezo-electric response amounted to 121 e.s.u./cm.$^2$

The value of $P_0$ obtained from the hysteresis loops is only approximate because of the assumptions involved in its determination. It cannot, moreover, be fixed definitely enough to be put down as a physical constant of Rochelle salt because it varies with different specimens, besides changing with temperature, pressure and fatigue. The value $P_0 = 30$ e.s.u./cm.$^2$ is thought to be a representative value and is checked by other measurements. The writer would not be surprised, however, to find other specimens giving several times this value. The change in polarization due to pressure however is derived by a differential method eliminating much of the uncertainty in measurements on one loop. The result in this case should be fairly definite, as indeed it seems to be.

Piezo-electric activity depends on both the crystalline structure and on the polarization. It is greatest for a polarization somewhat larger than normal and decreases in both directions for changes in this quantity, the polarization being changed by applying an electric field. It has been shown by the writer that this relation between activity and applied field is approximately like that of the derivative $\partial D/\partial E$ of the curve relating the dielectric displacement $D$ and the electric field $E$ of the crystal used as a condenser. Since this latter relation is in the form of a hysteresis loop it follows that the activity is also a double-valued function of the applied field depending on the direction of variation of the field. A curve illustrating this effect is reproduced in Fig. 2. The readings were taken in as short a time as possible to eliminate fatigue. These curves show that the piezo-electric response at zero field depends on the previous electrical treatment of the crystal. The latter fact has also been noted by W. G. Cady in the report previously referred to.

This after-effect does not persist very long but dies off exponentially with the time. The piezo-electric response or ballistic throw of the galvanometer for 250 grams has been observed to return to half value in 1 minute and to normal in over 20 minutes after fields of 150 volts have been applied for 3 minutes previously. There is a much greater after-effect in the direction of increased activity.

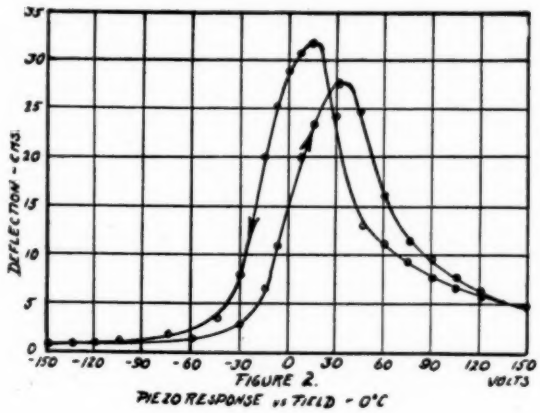



Fig. 2.

A corresponding dielectric effect is indicated by the double value of the condenser charge at zero field in the hysteresis loops. This is clearly due to a fatigue in the polarization and it also dies off exponentially with time. Herein is probably found the explanation of the "storage battery effect" described by W. G. Cady who observed that after applying a field of 100 volts for some time there was, on removal of the field, a small current which decreased gradually and flowed from the crystal as from a miniature storage battery.

The piezo-electric fatigue may well be a direct result of the fatigue in the polarization, as there seems to be a close relation between piezo-electric activity and polarization. It appears that the activity is approximately proportional to the rate of change of polarization with applied field and hence proportional to the dielectric constant. An examination of the temperature variation of the two quantities leads to this conclusion. It is further confirmed as regards field variation by the fact that the relation of activity to applied field is like $\partial D/\partial E$ vs. $E$ where $\partial D/\partial E$ is merely the instantaneous value of the dielectric constant $\kappa$. As an approximation we can write the piezo-electric modulus $\delta$ proportional to $\kappa$:

$$\delta = A \cdot \kappa.$$

If this equation were exact $A$ would be a fundamental piezo-electric constant of the substance, being of the order of $1 \times 10^{-7}$ between $-20°$ C. and $+20°$ C. At some temperatures and for some exceptional specimens the relation does not seem to be so simple.

## Effect of Moisture on Piezo-electric Properties.

In order to investigate the effect of dryness on the activity of Rochelle salt, some phosphorus pentoxide was enclosed in the chamber containing the crystal. The crystal soon started to dehydrate and after a few days was covered by a white coating. The piezo-electric throw for a load of 250 grams continually diminished. When the response was tested at different fields a more interesting fact was observed. Besides the decrease in response, the maxima were displaced along the field axis into a condition of greater polarization. This is shown by Fig. 3, the curves

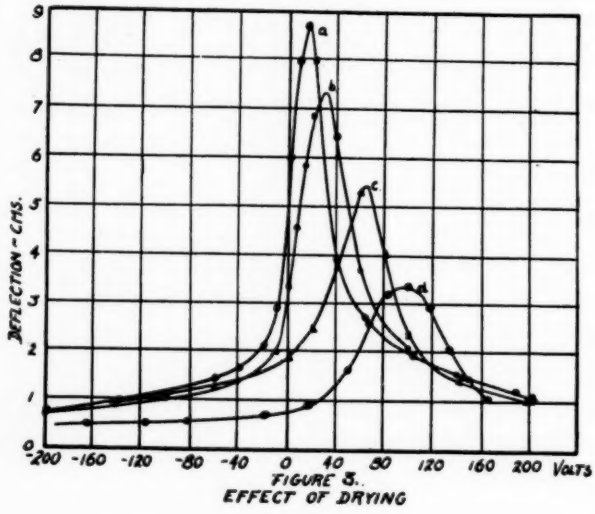



Fig. 3.

being taken after the lapse of the following times: (*b*) 1 day, (*c*) 3 days, (*d*) 12 days.

The decrease in the maxima and also their displacement is in the same direction as, and may be entirely due to, the effect of different dielectric properties of the crystal and of the dehydrated layer. In other words the presence of a layer of inactive dielectric of relatively low specific inductive capacity will diminish the charge on the plates due to the polarization of the central active layer, and thus decrease the piezo-electric response. It will also diminish the effective field across the active layer making it necessary to increase the potential difference

between the plates to produce the same field across the inner layer, thus shifting the position of maximum activity. The effects due to uniform layers can be readily calculated. Let $P_0$ be the polarization produced in the middle layer by pressure, let $P_1$ and $P_2$ be the electrically induced polarizations in the dielectrics 1 and 2 respectively (Fig. 4). Since the dielectric displacement is solenoidal we have:

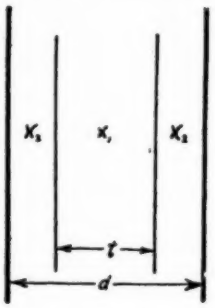



Fig. 4.

$$D' = E_1 + 4\pi P_1 + 4\pi P_0 = E_2 + 4\pi P_2 = 4\pi\sigma.$$

Since

$$P_1 = (\kappa_1 - 1)E_1 \qquad \text{and} \qquad P_2 = (\kappa_2 - 1)E_2$$

we can write

$$D' = \kappa_1 E_1 + 4\pi P_0 = \kappa_2 E_2.$$

The difference of potential between the plates is zero so that, replacing $P_0$ by $\sigma_0$:

$$0 = E_2(d - t) + E_1 t$$
$$= \frac{4\pi\sigma}{\kappa_2}(d - t) + \frac{4\pi}{\kappa_1}(\sigma - \sigma_0)t,$$

giving:

$$\frac{\sigma}{\sigma_0} = \frac{Q'}{Q} = \frac{\kappa_2 t}{t(\kappa_2 - \kappa_1) + \kappa_1 d}.$$

This gives us a relation between the piezo-electric response at zero field of the crystal with the dry shell and of the same crystal before it dried. The assumption is made that the elasticity of the shell is equal to that of the crystal so that a given total force produces the same polarization in the crystalline portion.

The position of the maximum will be changed to another value of total potential difference on the crystal. Let $V$ be the total potential drop and $V'$ be the drop across the crystalline part. When there is no dehydrated layer present

$$V = V' = dE,$$

where $E$ is the field strength in the dielectric. When there is a layer of uniform thickness $(d - t)/2$ on both faces then

$$V = (d - t)E'' + tE',$$

where $E''$ and $E'$ are the field strengths in the dielectrics 2 and 1 respectively. The dielectric displacement

$$D = \kappa_2 E'' = \kappa_1 E' + 4\pi P_0,$$

is solenoidal, and we can eliminate $E''$ from equations above and write:

$$V' = dE = (d - t)\frac{\kappa_1}{\kappa_2}E' + tE' + 4\pi P_0\left(\frac{d - t}{\kappa_2}\right).$$

Since the last term is small compared to the rest of the expression, this gives:

$$\frac{E'}{E} = \frac{\kappa_2 d}{t(\kappa_2 - \kappa_1) + d\kappa_1}.$$

The following quantities were measured and substituted in these equations.

$$\kappa_1 = 1000, \qquad d = 0.22 \text{ cm.},$$
$$\kappa_2 = 180, \qquad t = 0.14.$$

The quantity $t$ is an average obtained by breaking the crystal in several places and it is probably not very accurate because of the irregularity of the outer layer. We should, however, get a rough check on the plausibility of the proposed explanation. We find that

$$\frac{Q'}{Q} = 0.24$$

and that

$$\frac{E'}{E} = 0.38.$$

While the values of $Q'/Q$ and $E'/E$ from the maxima of curves $a$ and $d$ of Fig. 3 are respectively 0.39 and 0.33. The agreement is not as good as could be desired even after making allowance for the difficulties in estimating $t$. Possibly there is a true humidity effect with respect to piezo-electric activity but the above shows, at least, that it is quite small.

### PIEZO-ELECTRIC ACTIVITY AND TEMPERATURE.

In order to investigate the variation of activity with temperature, the chamber holding the crystal was immersed in $CO_2$ snow. After everything was thoroughly cooled and at $-75°$ C., the chamber was allowed to heat up. Above $-35°$ C. an electric heater was used. It was wound on a glass jar and insulated from the crystal chamber by a felt jacket. This jar was immersed in an oil bath to steady the heating rate while the felt eliminated any rapid changes of heating of the crystal. The current was gradually increased so as to keep the rate of heating uniformly between $\frac{1}{2}°$ and $1°$ C. per minute so as to eliminate thermoelastic stresses. The temperature was measured by means of a copper-constantan thermocouple directly soldered to an electrode on the crystal. In this way the actual temperature of the crystal itself was measured.

When the piezo-electric response or galvanometer throw for 250 grams was measured at the various temperatures for the first specimen the curve of Fig. 5 was obtained. This was duplicated to check the second

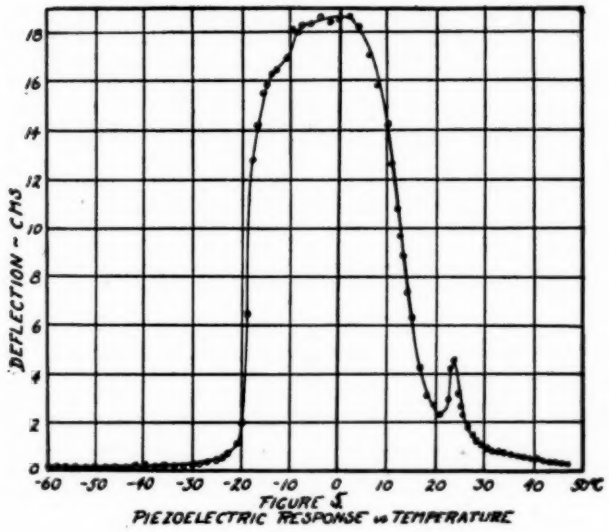



Fig. 5.

maximum. At − 70° C. the piezo-electric activity is comparatively negligible. As the temperature is raised slowly the activity stays small until − 30° C. is reached. At − 20° C. it is rising very rapidly, reaching a maximum at about 0° C. It decreases again but at 23° C. comes to a small but sharp maximum from which it diminishes slowly, becoming very small at + 50° C. The magnitude of the second maximum varies with the temperature at which heating begins. This second maximum was found in the case of two crystal plates provided with tinfoil electrodes attached by shellac.

Three other crystals were prepared with electrodes of mercury held against the crystal by two rectangular cups attached by wax. The thermocouple wires were immersed in the mercury. None of the crystals so prepared gave the second maximum. Moreover, none of them were as active as those used above. The variation of piezo-electric response of these specimens is shown in Fig. 6. The increase at − 30° to − 15° C. and the decrease at + 20° C. to + 30° C. are remarkably consistent. Between − 15° and + 20° C., however, they each show different characteristics. These mercury electrode crystals seemed to give more constant results than the crystals with tinfoil electrodes attached by shellac.

It was then suspected that the increased response of the crystal with

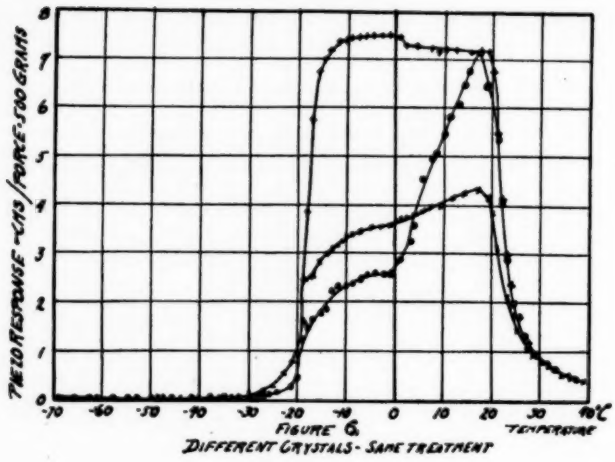



FIGURE 6.
DIFFERENT CRYSTALS - SAME TREATMENT

Fig. 6.

tinfoil electrodes and the presence of the second maximum was in some way due to the penetration into the crystal of the alcohol solvent of shellac. Accordingly one of the crystals originally with mercury electrodes was provided with the other type. As soon as the shellac was sufficiently dry, Curve *b*, Fig. 7 was obtained, the response originally

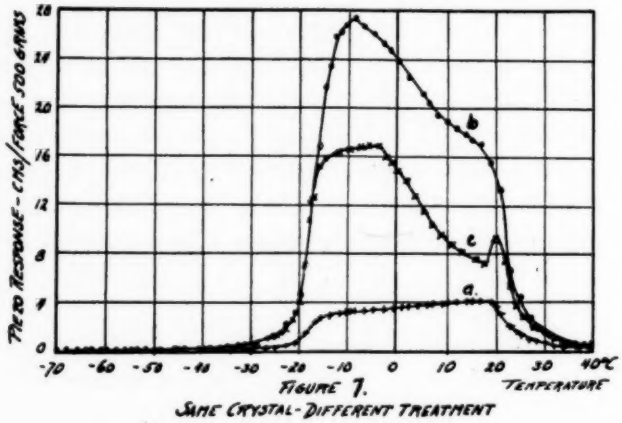



FIGURE 7.
SAME CRYSTAL - DIFFERENT TREATMENT

Fig. 7.

having followed Curve *a*. The sensitivity increased seven-fold at some temperatures but there was no second maximum. In two weeks the characteristics had changed to those shown in Curve *c*, seemingly checking the suspicion that alcohol was responsible for the second maximum and for the increased sensitivity. It would be interesting to use alcohol cup electrodes and investigate the continuous effect of alcohol soaking into the crystal. The effect is probably not chemical.

In a paper on the piezo-electric effect on Rochelle salt, A. M. Nicolson[1] describes a method for desiccating the crystals by soaking in alcohol and heating, thus making them stronger and more sensitive. The writer is certain, from his work on the subject, that complete desiccation will make the crystal entirely inactive. In the above method, apparently, the treatment is not prolonged enough to completely dehydrate more than a shell around the crystal and its effectiveness may be connected with the penetration of the alcohol into the crystal. The heating at 40° C. may also be effective in allowing a rearrangement and recrystallization of some of the molecules or groups not properly oriented. W. G. Cady, as well as the writer, has observed that heating the crystal will usually increase its sensitivity permanently, although sometimes the reverse is true.

An interesting side-light on the temperature variation of piezo-electric activity is offered by a study of curves like that of Fig. 2 but at different temperatures. They show that the effect of temperature is not so much to change the piezo-electric activity as to shift the position of the maximum from one value of the field to another. This is probably connected with the variation of the dielectric constant with temperature which will be taken up presently.

The charging throws of the crystal used as a condenser show variations similar to those of the activity except that they do not tend to zero but to a constant value at the lower temperatures. The crystals giving the second maximum on the piezo-electric curve show a similar peculiarity here. The crystals with the mercury electrodes give more regular curves. At 20° to 25° C. the crystals of both types begin to conduct, causing a steady drift of the galvanometer. Experiments seem to indicate that Ohm's law holds at least approximately. The conduction was at first thought to be electrolytic because of the manner in which Rochelle salt melts. Instead of real melting it appears that the crystal dissolves in its water of crystallization which is set free at 55° C. The desiccated crystal, however, decomposes into a tarry product and emits heavy white fumes above 150° C., without melting. The dehydrated crystal also begins to conduct above 20° C., making it probable that electronic and not electrolytic conduction is observed.

Measurements of conductivity were made on the natural crystal at various temperatures up to its liquefying point. The values obtained after the conductivity was sufficiently large to use a Wheatstone bridge are as follows:

[1] A. M. Nicolson, Proc. Am. Inst. Ele. Eng., Vol. 38, p. 1315 (1919).

TABLE I.

| Temperature. | Conductivity. |
|---|---|
| Less than 43° C. | Less than $0.5 \times 10^{-8}$ mhos/cm³. |
| 43 | $0.5 \times 10^{-8}$ |
| 45 | $1.0 \times 10^{-8}$ |
| 47 | $0.3 \times 10^{-7}$ |
| 49 | $0.5 \times 10^{-7}$ |
| 51 | $0.5 \times 10^{-6}$ |
| 53 | $0.6 \times 10^{-4}$ |
| 54 | $1.7 \times 10^{-4}$ |
| 57 | $5.0 \times 10^{-4}$ |
| Greater than 57 | $5.0 \times 10^{-4}$ |

At temperatures below 20° the dry crystal is a fairly good insulator having a specific conductivity of $5 \times 10^{-12}$ mhos/cm.³ at 0° C. The conductivity decreases slightly at still lower temperatures. In all these measurements the surfaces were thoroughly dried by the presence of phosphorus pentoxide in the crystal chamber.

TABLE II.

| Temp. Cent. | Dielectric Constant. | | Piezoelectric Modulus. | |
|---|---|---|---|---|
| | *A* | *B* | *A* | *B* |
| −70 | 71 | 42 | $0.041 \times 10^{-5}$ | $0.017 \times 10^{-5}$ |
| −50 | 85 | 50 | 0.068 " | 0.017 " |
| −30 | 140 | 146 | 0.41 " | 0.065 " |
| −20 | 386 | 252 | 5.4 " | 1.08 " |
| −10 | 943 | 924 | 18.9 " | 6.07 " |
| 0 | 1,380 | 956 | 22.9 " | 6.75 " |
| 10 | 1,100 | 928 | 18.9 " | 7.42 " |
| 20 | 688 | 645 | 13.5 " | 8.10 " |
| 30 | 423 | 146 | 2.2 " | 1.08 " |
| | Conduction commences | | 0.41 " | 0.41 " |

Table II. gives values of the dielectric constants for a field changing from 0 to 880 volts/cm. and of the piezo-electric modulus $\delta_{14}$ for shearing stresses of 220 grams/cm.². The modulus $\delta_{14}$ is defined by the relation given by Voigt $\sigma_1 = -\delta_{14} Y_s$ where $\sigma_1$ is the surface density of charge and $Y_s$ is the shearing stress producing it. The given values are thought to be the most representative in each case. They are subdivided into two classes, according to whether the electrodes were tinfoil attached by shellac (column *A*) or mercury in direct contact with the crystal (column *B*). The former method is the most convenient to use in general practice, but the latter is thought to give more exactly the properties of Rochelle salt in the direction of the ă axis. The dielectric

constants are surprisingly large, a fact noticed by Pockels[1] who supposes that this is due to "internal conductivity." The writer however has measured separately the conductivity at these temperatures and is of the opinion that this is a true dielectric constant arising from polarization of the dielectric, and for this reason being so closely related to the piezo-electric effect. Because of the relatively low specific inductive capacity of the desiccated crystal it is thought that the high specific inductive capacity of Rochelle salt is partly due to the water molecule.

## Magnetic Analogy.

There seems to be a strong analogy between the behavior of Rochelle salt as a dielectric possessing hysteresis and having an exceptionally large dielectric constant, and the phenomena of ferromagnetism. Accordingly some of the features of Weiss's theory of magnetism may find their counterpart in the phenomena in Rochelle salt. Weiss[2] plots the susceptibility against the reciprocal of the absolute temperature and finds that the curve may be represented by a succession of straight lines. He interprets the sudden changes in slope as due to changes in the number of magnetons. If the data of Figs. 8*a* and 12 are plotted against the reciprocal of the absolute temperature one likewise gets what may be considered to be a succession of straight lines. Actually however there occur rounded corners where the curves suddenly change direction. This may be due to slight non-uniformity in heating which occurred in spite of the precautions taken. It is considered that the straight portions are at least as definite as those shown in Weiss's paper. The most abrupt changes are at $-20°$ C. and at $+20°$ C. These may accordingly be considered as the "Curie points" in Rochelle salt.

## Relation to Optical Properties.

Some of the optical properties of Rochelle salt can be at least approximately found from the electrical data given. In the course of this calculation it is of course necessary to introduce some assumptions notably as to the nature of the permanent polarization. If one knew just how the permanent polarization was produced he could find the free period of this mechanism. The data needed are the force per unit displacement $f$ and the mass $m$ of that part of the molecule. The wave-length corresponding to the free period is given by the expression

$$\lambda = 2\pi c\sqrt{\frac{m}{f}}$$

$c$ being the velocity of light.

[1] Pockels, Lehrbuch der Krystaloptik, p. 508.

[2] P. Weiss, J. de Physique, Vol. 1, p. 968 (1911).

Let us assume for simplicity that only one electron is involved in the creation of the permanent moment. The quantity $f$ can be derived from the value of the permanent moment $P_0 = 30$ e.s.u./cm.$^2$ and from the displacement of the electron producing it. Since the force on an electron inside a dielectric of polarization $P_0$ is roughly equal to $\frac{1}{3}P_0e$[1] the expression for the wave-length may be put in the form:

$$\lambda = 2\pi c\sqrt{\frac{3md}{P_0e}}.$$

The value of $d$, the displacement of the electron, can be found as follows:

Taking 30 e.s.u./cm.$^2$ as the natural polarization, the moment per molecule is obtained by dividing by the number of molecules per c.c., the result being $7.1 \times 10^{-21}$ e.s.u. In each of these molecules there are 140 electrons, this being the sum of the atomic numbers of the constituent elements in Rochelle salt. If we suppose as above that only one of these is effective in producing the piezo-electric moment, its displacement from the center of force of the rest of the molecule will be $d = 2.7 \times 10^{-11}$ cm. It would of course be more reasonable to suppose that at least several of the electrons are displaced by different amounts, and to the extent that we do this the value calculated above becomes smaller.

Using these values of $P_0$ and $d$ for the simple case treated above we find for the wave-length the value:

$$\lambda = 4.2\ \mu.$$

Coblentz[2] shows the presence of fairly strong absorption in this region of the infra-red. This may, however, be due to the water of crystallization and not to the cause cited above. These two possibilities should be distinguishable experimentally because the character of the absorption due to these electrons should change greatly with the temperature, as the piezo-electric elasticity or force per unit displacement of the electrons changes.

The natural period as found above should be the same as that involved in rotatory dispersion formulæ, since both the piezo-electric effect and optical rotation are due to an unsymmetrical or twisted structure of the molecule. J. J. Thomson[3] gives an approximate formula for the specific rotation, namely:

$$\rho = \frac{e^2dp^2}{c^2Mmn^2},$$

[1] H. A. Lorentz, Theory of Electrons, p. 306.
[2] W. W. Coblentz, Infra Red Spectra, Vol. 2, p. 38.
[3] J. J. Thomson, Phil. Mag., Dec., 1920.

in which $e$ is the charge of the electron, $c$ is the velocity of light and $M$ and $m$ are the masses of the molecule and of the electron, $d$ is the radius of the molecule, $p$ is the free period, and $n$ is the frequency for which $\rho$ is to be calculated. Using the value of $p$ derived from piezo-electric data we find for sodium light the specific rotation of the order of magnitude of 10°, the tables giving 22.1°. Considering the fact that so little is known of the structure of the Rochelle salt molecule, the approximation is fair.

The writer is indebted to Professor W. F. G. Swann, who initiated this research and gave many helpful suggestions, and to Dr. W. R. Whitney, Director of the Research Laboratory of the General Electric Company, whose presentation of two beautiful crystals made the work possible.

Physical Laboratory,
University of Minnesota.

# MINIMUM SOUND ENERGY FOR AUDITION FOR TONES OF HIGH FREQUENCY.

BY C. E. LANE.

SYNOPSIS.

*Minimum Energy for Audition for Tones above 2000 p.p.s.*—Using the new tone generator developed by Hewlett as the source of sound, experiments were carried on at night and out of doors on a platform raised 5 meters above the ground and with the listening ear 150 cm. from the source. The amplitude of vibration of the diaphragm of the generator was calculated from the electrical input, and from it the corresponding sound intensity at the ear of the listener was computed, assuming the amplitude of the sound wave at the diaphragm the same as that of the diaphragm and correcting for the concentration of sound around the axis of symmetry as experimentally determined. No correction for the effect of the listener's head, however, was made. *Sensitivity frequency curves* for eight normal ears, ages 19 to 35 years, are reproduced. The minimum audible intensity was found to remain practically constant at $7 \times 10^{-3}$ ergs per cm.$^2$ for frequencies from 2,000 to 14,000 p.p.s., but above 14,000 the sensitivity decreased more and more rapidly until at between 18,000 and 20,000 p.p.s., depending on the individual, an intensity of 0.1 erg per cm.$^2$ was inaudible. *A variation with age* was observed, the upper frequency limit being considerably higher for children and lower for older persons than for normal young adults.

*Distribution of Sound Intensity around a Hewlett Tone Generator for 2,000 to 15,000 p.p.s.* was determined roughly by studying the minimum amplitude for audition as a function of the angular position of the listener with reference to the axis of symmetry. The sound is largely concentrated in a cone of about 20°, the angle decreasing as the frequency increased, so that for 10,000 p.p.s., for instance, the intensity 150 cm. along the axis was fifty times as great as if the distribution had been spherical.

## INTRODUCTION.

THE purpose of this investigation was to determine in absolute units the sensitivity of the ear for tones ranging from 2,000 p.p.s. to the upper limiting audible frequencies. Experiments have been made by many different observers for determining the minimum amount of sound energy for audition but most of these investigations have been concerned with tones of frequencies below 4,000 p.p.s. Little work at the higher frequencies has been done because of the limitations of the apparatus used. In the early work done by Wien[1] and in the recent work of Kranz[2] the ear was shown to reach a maximum sensitivity in the neighborhood of 2,000 p.p.s. At the Chicago meeting of the National Academy of Sciences, November 14, 1921, Fletcher and Wegel presented some results

[1] Archiv. für die gesamte Physiologie, Vol. 97, pp. 1–57, 1903.

[2] PHYS. REV., (2) xvii, 1921, page 384.

which they had obtained for sensitivity of normal ears. These results showed that the ear reached a maximum sensitivity in the neighborhood of 2,000 p.p.s. and then remained constant to 4,000 p.p.s. No attempt was made by them to obtain measurement in absolute units at higher frequencies.

## Apparatus and Method.

In this investigation the new tone generator,[1] developed by C. W. Hewlett, was used as a source of sound. The radiating surface of the tone generator consisted of a thin aluminum diaphragm, 10 cm., in diameter, actuated by a flat coil carrying variable polarizing (direct) and alternating currents. One side of the diaphragm was wholly unobstructed for the free passage of sound waves from its surface, while the type of coil used did not greatly affect the passage of sound from the opposite side. Amplitudes of motion of the diaphragm for minimum audible sounds were calculated from the corresponding current input by using Hewlett's theory, adapted to suit the particular arrangement used. At any frequency it can be shown that the amplitude of motion of the diaphragm is proportional to the product of the direct and alternating currents and that the energy radiated is proportional to the square of this product.

The work was done out of doors with the observer on a small platform five meters above the ground and the sound source 1.5 meters from his ear. This arrangement was assumed to reduce reflections from the ground to an amount negligible compared to the energy received directly. It is evident that the ratio of direct energy from the apparatus to reflected energy from the ground, assuming the most unfavorable conditions, would be of the order of magnitude of the ratio of $(2 \times 5)^2 : 1.5^2 = 44 : 1$.

The work was done at night to minimize the interfering effect of noise. The face of the sound source was turned toward the observer and the ear to be tested was turned toward the source. It was found by trial that it was not necessary to close the other ear on account of the sound shadow of the head.

The amplitude of the sound wave was assumed to be the same at the diaphragm surface as that of the diaphragm. The total energy emitted was calculated assuming it to be the same as would be radiated in a plane wave. Therefore, the total amount of sound energy, $E_t$, given off by one side of the diaphragm per second would be given by—

$$E_t = \tfrac{1}{2} S \rho V A^2 \omega^2.$$

$S$ = area of each side of the diaphragm.

[1] Phys. Rev., (2), xix, p. 52, 1922.

$\rho$ = density of the air.
$V$ = velocity of sound in air.
$A$ = amplitude of vibration of the diaphragm.
$\omega$ = $2\pi$ times the frequency.

In a simple spherical distribution the energy flux per sq. cm. at a distance of $D$ from the source would be $E_t/2\pi D^2$. This is an average value for energy flux on the surface of a hemisphere of radius $D$. If $R$ is the ratio of the actual value, $J$, at the position of the observer's ear to the average value, then

$$J = \frac{E_t R}{2\pi D^2}$$

$R$ was determined for each frequency from the following considerations.

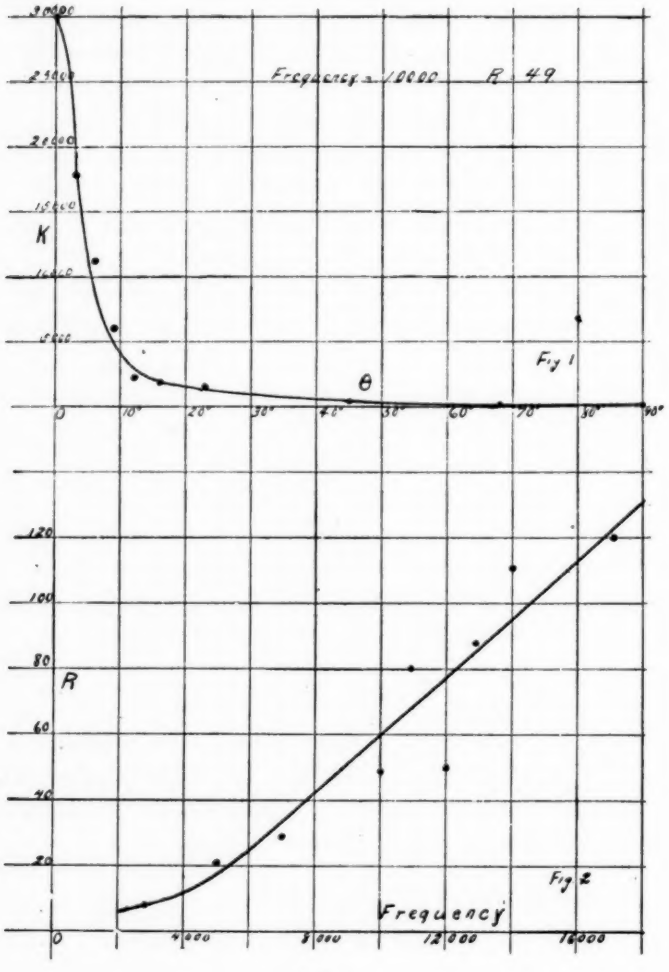



Fig. 1.
Fig 2.

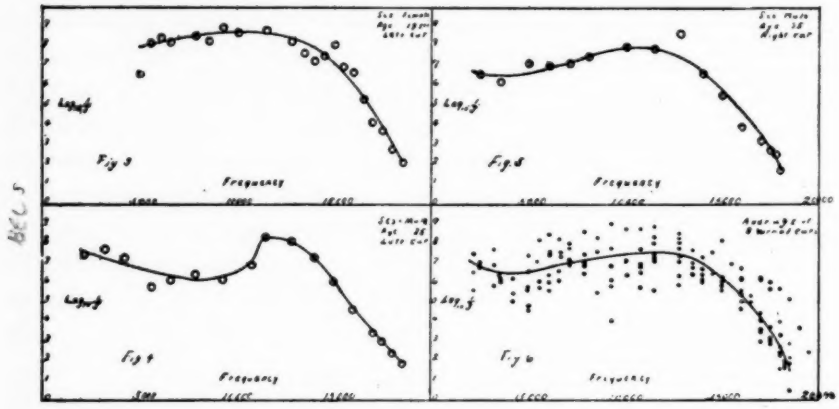
The sound field was assumed to be symmetrical with respect to the axis of the diaphragm. This axis (horizontal) also passed through the ear of the observer. The relative distribution of energy flux on the surface of a sphere of radius $D$ was determined by calculation from the measurement of minimum audible amplitude of the diaphragm as it was turned about a vertical axis, through its center, through an angle of 180°. Fig. 1 shows energy density so determined at 10,000 p.p.s. plotted in arbitrary units as a function of the angle. Between 90° and 180° it is roughly symmetrical with that between 90° and 0°. It is seen that the major part of the energy from the side of the receiver toward the observer is concentrated within a cone making an angle of 20° at the center of the diaphragm. The assumption that all of the energy radiated from one side of the diaphragm is contained in the corresponding beam indicated in Fig. 1 is justified on the basis of the theory of radiation of a plane wave from a circular aperture. Using this distribution curve and the calculation of the total energy flux, as determined from the tone generator theory, the energy flux per sq. cm. could be calculated at any point on the sphere of radius $D$. The ratio, $R$, of the energy flux density at the position of the ear to that which would be obtained in a simple spherical distribution was found to be 49 : 1 at the frequency illustrated in Fig. 1. Fig. 2 is a plot of $R$ as a function of frequency. This shows, as might have been expected, that the energy becomes more and more concentrated in a narrow beam as the frequency increases.

## RESULTS AND CONCLUSIONS.

The value of $J$ was determined at different frequencies for eight normal ears. In order to show the variation in sensitivity of the ears graphically the $\log_{10}(1/J)$ was plotted against frequency. Logarithms were necessary because of the wide variation of sensitivity of the so-called normal ears. The audiograms—sensitivity frequency curves for the ears—thus obtained are shown in Figs. 3, 4, 5 and 6. Figs. 3, 4 and 5 are audiograms for individual ears, Figs. 4 and 5 being the left and right ears of the same individual. Fig. 6 shows the results obtained for eight ears from seven different individuals. Each of the persons from whom the data were obtained was between 19 and 35 years of age. The value of $J$ for a frequency of 2,000 p.p.s. as obtained by taking the mean value of $\log_{10}(1/J)$ for this frequency, was found to be $7 \times 10^{-8}$ ergs. This is about three times the value given by Kranz, about seven times the value obtained by Fletcher and Wegel[1] and 30,000 times the value given by Wien for the same frequency. But little variation in the ear sensitivity

[1] R. M. S. pressure in dynes per sq. cm. is equal to 6.5 $\sqrt{J}$.

from this was noted until a frequency of 14,000 p.p.s. was reached. As the frequency was increased above 14,000 p.p.s., the sensitivity decreased more and more rapidly. Between 18,000 p.p.s. and 20,000 p.p.s., a frequency was reached for each individual ear at which it was no longer



Figs. 3, 4, 5, 6.

possible to produce a tone of sufficient intensity for audition by means of the apparatus used. The mean value for $J$ at a frequency of 18,500 was about .1 erg. If it had been possible to produce tones of greater intensity, no doubt the threshold of audition would have been found at a higher frequency. However, it would appear from the rapid decrease in sensitivity at these high frequencies, it would be necessary to increase the intensity of the tone by a very large amount in order to raise the threshold to a frequency noticeably higher.

Special attention is called to the age of the individuals tested. There is certainly a great variation in ear sensitivity, especially for high frequencies, with the age of the individuals. Some qualitative results were obtained which show that children under fifteen years of age may hear tones as high as 25,000 cycles when the intensity is no greater than for a value of $J$ corresponding to .1 erg. On the other hand, persons past fifty years of age are not able, as a rule, to hear such high frequencies as were heard by the individuals whose ears were tested.

There are a few sources of inaccuracy in the results obtained which should be mentioned. The value of $R$ varies a great deal from the mean value. However, this error is small and may be neglected when we consider the fact that the observational errors for the same frequency and the same individual may themselves vary by as much as 50 per cent. It should also be mentioned here that the work was not done under

perfectly quiet conditions and the very slight disturbance would make the ear appear less sensitive than it actually is. The work was done at night but some noise was present due to the sound of insects. $J$ has been defined as the amount of sound energy necessary for audition flowing per second through a sq. cm. It is evident that the value of $J$ obtained by this method only gives the amount of energy which would flow through a sq. cm. were the head not at the position for which $J$ was calculated. Further, if it may be assumed that the sound is completely absorbed by the head, the figures given for sensitivity represent the energy per sq. cm. flowing into the ear. If the head may be assumed to be a plane reflector the actual energy density at the ear is twice that in the first case. The actual condition is between the two extremes but in all probability nearer the second. However, it will be seen from the figures that a factor of two would involve a negligibly small relative error.

In conclusion I wish to express my appreciation of the assistance rendered during the experimental work by Dr. C. W. Hewlett and other members of the staff of the University of Iowa as well as the suggestions offered in the interpretation of the data by various members of the scientific staff of the Western Electric Company, Inc.

Physics Laboratory,
State University of Iowa,
June, 1921.

# THE SENSITIVITY AND PRECISION OF THE ELECTROSTATIC TRANSMITTER FOR MEASURING SOUND INTENSITIES.

BY E. C. WENTE.

SYNOPSIS.

*Electrostatic Transmitter of Constant Sensitivity.*—(1) *Characteristics.* This instrument is the same in principle as that described in 1917, but certain changes have been made which, as proved by actual tests, render the sensitivity independent of changes of temperature, pressure and humidity. The sensitivity is also found to be constant over a long period of time. By means of a piston-phone and a thermophone, for which corrected formulæ are available, both the absolute sensitivity and phase lag were determined for frequencies of from 10 to 12,000 cycles. Eight transmitters similarly constructed give the same curves within 20 per cent. With a steel diaphragm 0.0051 cm. thick having a natural frequency of 7,000 cycles, and with an air gap of 0.0025 cm., the mean sensitivity is about 0.35 millivolt/dyne. (2) *Use with an amplifier for measurement of sound intensity.* Combined with an amplifier of ordinary design the instrument has an over-all sensitivity which is practically uniform from 25 to 8,000 cycles. It is therefore remarkably well adapted for the measurement of the intensities of complex tones and tones of changing pitch and for use with an oscillograph for recording sound waves. On the other hand, if sounds of a definite pitch are to be measured, the apparatus can be made highly selective and almost any desired sensitivity can be obtained by using a tuned amplifier in connection with a vibration galvanometer.

THE writer some years ago published a paper[1] in this journal on the use of an electrostatic transmitter for the absolute measurement of sound intensities. The transmitter, as there described, consisted essentially of a thin metal diaphragm under tension separated by a small distance from a plane metal plate, the plate and the diaphragm forming the two electrodes of an air condenser. Data were given which showed that the instrument had a uniform sensitivity over a wide range of frequencies and so was especially adapted for the measurement of intensities of sounds of various frequencies.

The relation between sensitivity and frequency was determined by means of a thermophone and also, at the lower frequencies, by means of a piston-phone. But, as the two methods did not yield the same absolute values, doubts were cast upon the accuracy of the results. Since then the theory of the thermophone has been further developed and corrected formulæ for its acoustic efficiency have been obtained.[2] The pressures calculated by these new formulæ have been found to agree with those

[1] Vol. X., No. 1, p. 39, July, 1917.

[2] E. C. Wente, PHYS. REV. (2), XIX, p. 333 ~~666~~.

given by a piston-phone, so that an absolute calibration of a transmitter may now be made with the thermophone which is dependable over a wide frequency range.

The particular electrostatic transmitter described previously had a natural frequency of nearly 17,000 cycles per second. As this frequency is considerably beyond the region which is covered in most acoustic measurements, it is desirable to construct an instrument with a lower natural frequency and thereby obtain greater sensitivity. Dr. I. B. Crandall [1] has shown theoretically how the natural frequency and damping of an electrostatic transmitter may be given almost any desired values by cutting grooves of the proper size in the back plate.

The transmitter which is here described has a natural frequency slightly over 10,000 cycles per second and a damping constant of 14,000. The sensitivity-frequency characteristic is such that an amplifier may readily be constructed so that the sensitivity of the amplifier and transmitter combined shall be nearly the same from 25 to 8,000 cycles per second. Tests have shown that the sensitivity of the transmitter is closely maintained under various atmospheric conditions for a long period of time.

## CONSTRUCTION OF THE TRANSMITTER.

A sectional drawing of the transmitter is shown in Fig. 1. The transmitter differs from the instrument previously described in several essential respects. The diaphragm, *A*, is made of 0.002 inch (0.0051 cm.) steel and is stretched so that its natural frequency in free air is 7,000 cycles per second. Annular grooves are cut into the face of the back-plate, *B*, to give the diaphragm the desired natural frequency and damping. The length of the air-gap is 0.001 inch (0.0025 cm.). To keep out moisture, the space surrounding the back-plate is sealed off completely from the outside air. A thin rubber diaphragm, *C*, is provided to keep the pressure on the two sides of the steel diaphragm substantially equal under all conditions of temperature and atmospheric pressure.

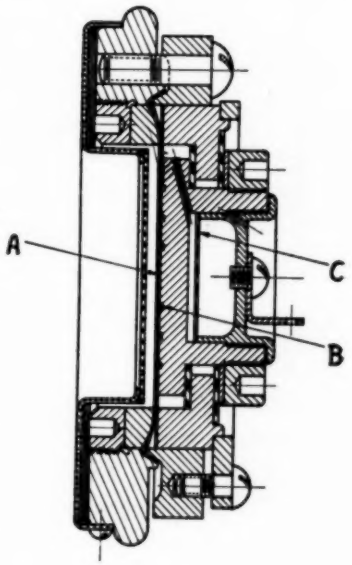



Fig. 1.

Sectional view of the electrostatic transmitter.

[1] ~~E. C. Wente~~, PHYS. REV., (2) XI., 450 (1918).
I.B. Crandall

## CALIBRATION OF THE TRANSMITTER.

The open-circuit voltage of the transmitter per unit of pressure has been measured with the piston-phone for the frequency range of 10 to 200 cycles per second and with a thermophone for the frequency range of 60 to 12,000 cycles per second. Both of these instruments have been described in another paper.[1] The method of measurement was virtually the same as previously described,[2] except that an a.c. potentiometer[3] was used in place of a thermo-couple and galvanometer. The polarizing voltage in all cases was 200.

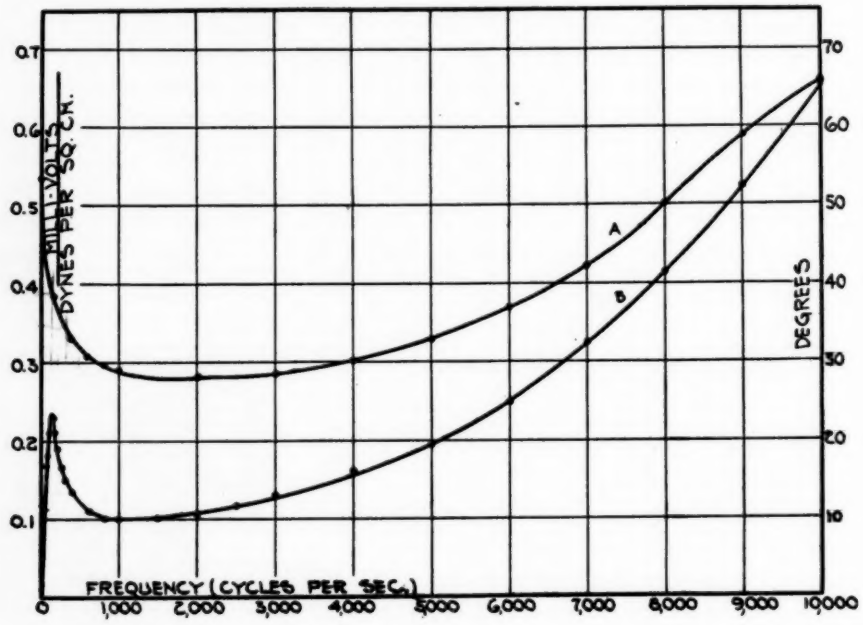



Fig. 2.

Sensitivity-frequency characteristic of the electrostatic transmitter. *A*. Volts per unit of pressure. *B*. Phase lag of e.m.f. behind pressure.

Fig. 2 gives the calibration curve obtained by averaging the results for eight transmitters. Between 25 and 8,000 cycles the calibration curve of none of the individual transmitters differs from this average curve by more than 20 per cent. To make all the transmitters exactly alike would require extreme precautions in construction, which would add considerably to their cost. However, even if there is a considerable variation in the mechanical constants of the individual instruments, we

[1] E. C. Wente, The Thermophone, loc. cit.

[2] E. C. Wente, PHYS. REV., (2) X., 51 (1917).

[3] E. C. Wente, Journal A. I. E. E., XL, p. 900, 1921.

may obtain a very nearly correct value of the calibration curve of any particular instrument by measuring the sensitivity at 200 cycles with the piston-phone and multiplying the ordinates of the curve given in Fig. 2 by the ratio of the value so obtained to the value of the ordinate of this curve at 200 cycles. For the eight calibrated transmitters the difference between the true calibration and the values obtained by this latter method was at no point greater than 12 per cent. for frequencies lying between 20 and 8,000 cycles per second, and for most of the transmitters the difference was nowhere greater than 5 per cent. This difference is small enough to be neglected in practically all acoustic measurements. Unless a precision greater than five per cent. is required it is therefore unnecessary to make any other measurements on transmitters of this type than that of the determination of the sensitivity at 200 cycles by means of the piston-phone, a measurement which may be made in a few minutes.

Fig. 2 shows that the sensitivity of the transmitter is not independent of frequency. However, since the transmitter is generally used with an amplifier, the sensitivity varies with the frequency in a desirable way. An amplifier as normally constructed has an amplification characteristic which is nearly proportional to the reciprocal of the efficiency characteristic of the transmitter. At any rate, an amplifier can readily be designed so that the sensitivity of the transmitter and amplifier combined is practically uniform from 25 to 8,000 cycles.

For the frequency range of 60 to 10,000 cycles a determination was also made of the phase relation between the pressure exerted on the diaphragm and the voltages generated by the transmitter. The values that were obtained are also plotted in Fig. 2. The maximum in the curve at 200 cycles is due to the fact that the damping of the diaphragm by the air in the gap increases with decrease in frequency.[1]

## Variation of Sensitivity with Time.

To determine the change in sensitivity of the transmitter with time under ordinary conditions of use it would be necessary to make measurements extending over a long period. The more practical method of subjecting the transmitter to a higher temperature for a shorter period of time was therefore adopted. A transmitter was heated daily for five or six hours to about 45° C. and then allowed to cool to room temperature. No change in efficiency was observable even after this process had been continued for more than two weeks. The precision of the measurements was about 2 per cent. The transmitter was then heated

[1] I. B. Crandall, loc. cit.

to 100° C. for several hours. After being allowed to cool it was again tested but no change in sensitivity was observable. It is thus reasonable to assume that under ordinary conditions the sensitivity will not change appreciably during the course of several years.

### EFFECT OF TEMPERATURE AND PRESSURE ON SENSITIVITY.

When a rigid plate was used in place of the flexible rubber diaphragm, *C*, and equalization of the static pressure on the two sides of the diaphragm thereby prevented, measurements with the piston-phone and electrostatic voltmeter showed that the sensitivity of the transmitter changed about 2 per cent. per degree Centigrade at 200 cycles. With the rubber diaphragm, however, within the temperature range of 20 to 40 degrees C. the total change in sensitivity was less than 2 per cent., which is negligible for all practical purposes. The principal reason for this small temperature coefficient lies in the fact that the instrument is constructed almost entirely of the same material. The clamping rings and the diaphragm have nearly the same temperature coefficient of expansion, so that any change in temperature will produce but little change in the tension of the diaphragm. The diaphragm, although thin, cannot assume a temperature very different from that of the frame, for it is separated by such a small distance from the back plate that heat can flow from one to the other nearly as readily as if they were in contact.

If there were no displacement of the rubber diaphragm a change in temperature of 20° C. would produce a difference in pressure on the two sides of the diaphragm equal to 7 per cent. of one atmosphere. It follows, therefore, that a change in atmospheric pressure as great as this will not change the sensitivity of the transmitter by an appreciable amount.

### COMPARATIVE SENSITIVITY OF THE TRANSMITTER.

The mean value of the sensitivity of the transmitter given above is approximately 0.35 millivolt per dyne. A more comprehensible idea of this sensitivity may be obtained from the fact that the male voice in ordinary conversation exerts a pressure of about 10 dynes per sq. cm. at a distance of 3 cm. from the mouth of the speaker.[1] With a three-stage amplifier, thermocouple and galvanometer pressures as low as 0.01 dyne per sq. cm. may be measured. If the tone is produced by some electrical device such as a telephone receiver and the source of current is supplied by an oscillator, an a.c. potentiometer may be used. In this case pressures may be measured which are barely perceptible to the ear.

[1] I. B. Crandall and D. Mac Kenzie, PHYS. REV. (2), XIX, p. 221.

## Concluding Remarks.

Little has been said about amplifiers in this paper although the electrostatic transmitter has little practical value unless it is used with an amplifier. Experiments have shown that the transmitter changes but little with time and atmospheric conditions. The amplifier, when properly designed and if the vacuum tubes are carefully chosen, will maintain the same value of amplification for a long period, provided the plate voltage and the filament current are kept at a constant value. An amplifier used in most of the experiments described above did not vary by more than a few per cent. during the course of several months. A combination of electrostatic transmitter and amplifier can thus be used as an absolute phonometer, the readings of which are dependable from day to day.

In the preceding discussion it has already been pointed out that one of the chief merits of the electrostatic transmitter is the fact that it has a very uniform response and so is especially adapted for measuring sounds of complex wave form or for comparing the intensities of tones of different frequencies. However, in some classes of problems it is desirable to have an instrument which is sharply tuned so that it will respond to a tone of one frequency and be unaffected by any other tones that may be present at the same time. If an electrostatic transmitter is connected to a tuned amplifier the output of which goes to a vibration galvanometer, selectivity of a very high order may be obtained and an amplifier of sufficient amplification may be used to give the combination almost any desired sensitivity.

Research Laboratories of the
American Telephone and Telegraph Company,
and Western Electric Company, Inc.

# REFLECTION OF X-RAYS FROM ROCK SALT.

BY BERGEN DAVIS AND W. M. STEMPEL.

SYNOPSIS.

*Reflection of X-rays from Rock-salt Crystals.*—By means of the double spectrometer arrangement previously used in studying the reflection from calcite, a narrow beam of nearly homogeneous rays from one crystal was reflected from a second crystal. The two natural cleavage surfaces used were obtained by splitting a good clear specimen. The *rocking curves* are irregular and more than 50 times as wide as corresponding curves for calcite, while the *per cent. reflection at parallelism* of the surfaces was much less than for calcite, being only 10 for 3° grazing angle and 5 for 7°. Polishing the reflecting surfaces increased the curve width somewhat but washing with water restored the surfaces to their original condition. By interposing a third slit between the crystals and moving it across the beam more detailed information was obtained as to the position and character of the imperfections in the crystal surface. Another selected pair of freshly split surfaces gave similar results, except that the per cent. reflection at parallelism was about twice as great.

*Imperfections of Rock-salt Crystals.—Compared with calcite,* rock-salt crystals are evidently very imperfect. The recent results of W. L. Bragg also prove this. The greater apparent reflectivity observed with rock-salt is due to the fact that its irregular structure reflects a much broader band out of a continuous x-ray spectrum.

IN a recent number of the PHYSICAL REVIEW (May, 1921) the authors presented some results of an investigation of the reflection of x-rays from calcite. This reflection was investigated by means of a double x-ray spectrometer so arranged that a nearly homogeneous beam of x-rays from the first crystal ($A$) was allowed to fall on a second crystal ($B$). Maximum reflection was obtained when the reflecting atomic planes of the two crystals were parallel. On rocking the second crystal about the position of parallelism interesting curves of energy distribution were obtained which were strikingly narrow, the width at half-maximum being as small as 16 seconds of arc in some cases.

A similar investigation has been made of the reflection from the (100) planes of rock-salt. The crystals were mounted on the double spectrometer as shown in Fig. 1. The reader is referred to the original paper for details of the spectrometer and the method of observation.

Two properties in particular of this reflection were investigated. (1) The degree of perfection or imperfection of the crystals as indicated by the width and regularity of the rocking curves. Imperfections in the surface of the crystals or slight local tilting of the reflecting planes have the effect of broadening the rocking curves very much. It was found in the case of calcite, that the more nearly perfect the crystal the nar-

rower and more regular the rocking curves. (2) The ratio of the energy at maximum reflection from the second crystal to the energy of the beam from the first crystal before reflection from the second one. This we call *per cent. reflection.* It is not a true coefficient of reflection, but would probably be the true coefficient for perfect crystals.

Two sets of rock-salt crystals were investigated, which are designated in the tables as crystals No. 1 and crystals No. 2. These crystals were the best that could be obtained from a supply house. They were large, fairly clear and nearly perfect as viewed by the eye. These crystals were split along (100) cleavage planes and mounted on the spectrometer in such position that the two reflecting surfaces were the contiguous planes before splitting. In the case of crystals No. 1 observations were made with the surfaces (*a*) split only, (*b*) polished, (*c*) washed with water.

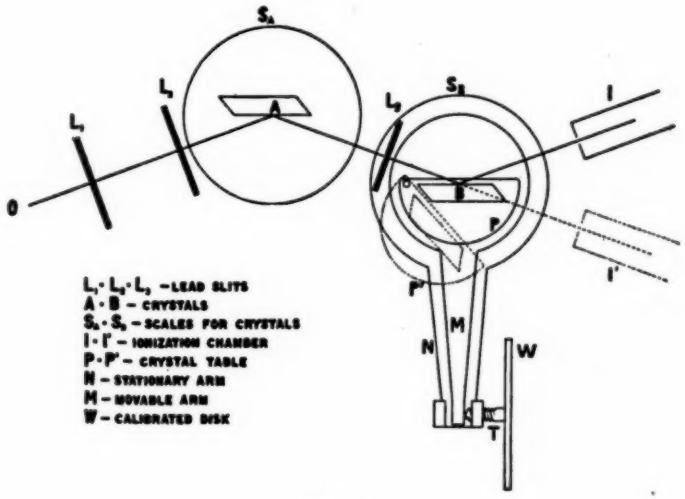
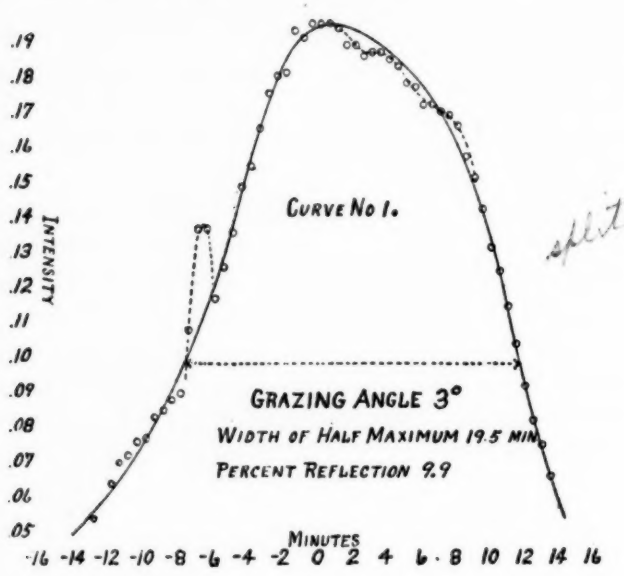



Fig. 1.

Three striking differences are observed between the results for rock-salt and for calcite. (*a*) The rocking curves for rock-salt are many times wider (more than 50 times) than those for calcite. (*b*) The rocking curves were irregular in outline and not symmetrical. (*c*) The per cent. reflection was much less than for calcite.

A third slit $L_3$ (width .4 mm.) was introduced between the crystals for the purpose of limiting the beam of x-rays to a portion only of the crystal surfaces (see Fig. 1). The types of rocking curves obtained for crystals No. 1, with the slit $L_3$ so placed as to limit the beam to a region near the center of the crystals are shown in curves Nos. 1, 2 and 3. The widths at half-maxima and the per cent. reflection for the several grazing angles are given in the table.




split only

Fig. 2.

These curves all show an irregularity occurring on the same side for all three grazing angles. *However, when the slit was removed so that the beam of x-rays covered nearly the whole of the crystal surfaces the irregularities were ironed out.* The curves were regular in outline but were somewhat unsymmetrical.

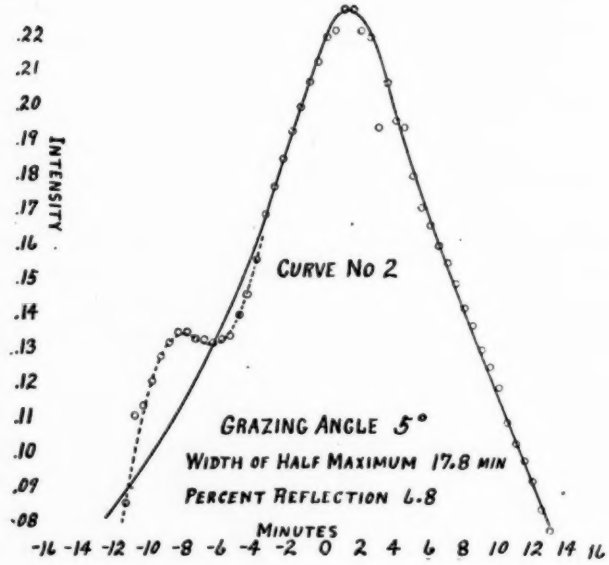



Fig. 3.

These results indicate that the crystals were quite imperfect. To check up these irregular effects, the slit $L_3$ was progressively moved to different positions across the beam of x-rays. The slit limited the reflection to a new portion of the crystal surfaces for each position. The successive positions of the slit were so adjusted that the regions on the crystals from which the rays were reflected were adjacent to one another. The results are given in the table for three positions $A$, $B$ and $C$. The rocking curves obtained, without the irregular humps, are given in Fig. 5.

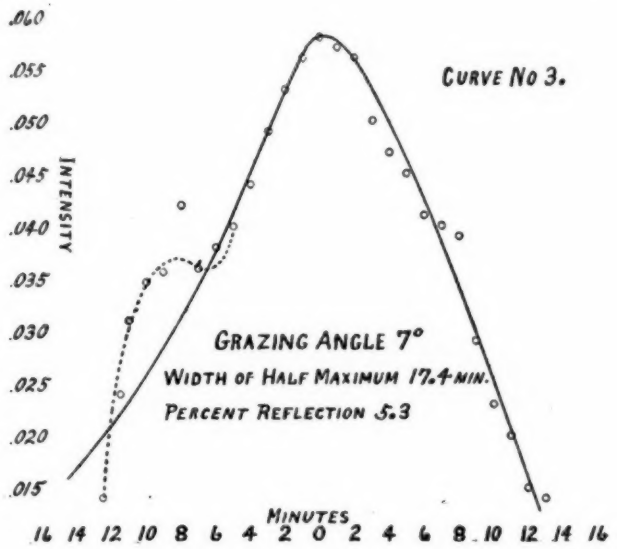



Fig. 4.

The curves $A$, $B$ and $C$ are given in the order of decreasing glancing angle. The angular position of the curves is displaced but not regularly, as the slit was progressively displaced across the beam. This means that the reflecting elements in the surface of the crystals did not lie in continuous planes, but that in certain regions the reflecting planes were tilted at a small angle to the planes near them. The greatest tilting for the two successive positions $A$ and $B$ was about 14 minutes of arc as indicated by the positions of the curves $A$ and $B$ in the figure. *Had the crystals been perfect these three curves would have been superimposed.*

The above results were obtained with the natural cleavage surfaces of the crystals. Polishing and etching of the surfaces had been observed to produce a great effect on the reflection and width of rocking curves in the case of calcite. The effect of polishing and washing the rock-salt crystal surfaces was investigated and the results are shown at the bottom of the table for crystals No. 1. Observations were made at only one

glancing angle. It will be observed that polishing increased the width of rocking curve to some extent, but that when the surfaces were washed with water to remove the polish they were restored to their original condition. No measurements were made of the per cent. reflection in this instance, as it was not desirable to disturb the setting of the instrument between the processes of polishing and washing.

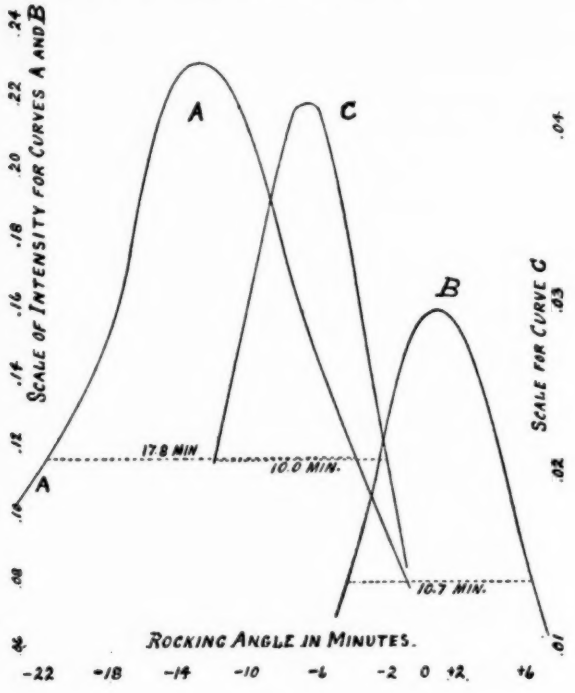



Fig. 5.

To further test this matter of irregular reflection, a new specimen of rock-salt was obtained. This was a large clear piece, in fact, nearly perfect as viewed by the eye. It was found, however, after splitting that the two cleavage surfaces showed small ripples and undulations when examined by reflected light. The crystal was split a number of times until fairly satisfactory surfaces were obtained.

Observations were made with this pair of crystals, (*a*) with freshly split surfaces, (*b*) with the surfaces both polished and washed. The results for three different glancing angles are given in the table for crystals No. 2.

The curve width is somewhat less than that first obtained with crystals No. 1, but is approximately the same as that obtained for No. 1, after the slit $L_3$ had been once removed and then replaced. It will be noticed

that polishing and washing did not affect the width of rocking curves materially.

The per cent. reflection for this pair of crystals was considerably greater than for the first pair (see column four of the tables).

The decrease in reflection for increase of wave-length was more marked for this pair than for the first pair of crystals.

TABLE I.

ROCK-SALT.

*Crystals No. 1 ($A_1$ and $B_1$).*

| Condition of Crystal. | Grazing Angle. | Width at Half-Max. | Per Cent. Reflect. |
|---|---|---|---|
| | | With Slit $L_3$ between Crystals. | |
| Split only..... | | 18.7 min. | 10.1 |
| | 3° | 19.9 min. | 9.9 |
| | | 19.3 min. | 10 |
| | | 16 | 8.9 |
| | 5° | 17.8 | 6.8 |
| | | 16.9 | 7.8 |
| | 7° | 17.4 min. | 5.3 |
| | | Without Slit $L_3$ between Crystals. | |
| Split only..... | 5° | 12.3 min. | 9.5 |
| | 7° | 11.7 | 7.6 |
| | 9° | 12.5 | 5.7 |
| | | Slit $L_3$ Moved across X-ray Beam. | |
| Split only—*A*..... | 5° | 17.8 min. | |
| *B*..... | 5° | 10 | |
| *C*..... | 5° | 10.7 | |
| | | With Slit $L_3$ between Crystals. | |
| Split..... | 5° | 10.4 min. | |
| Polished..... | 5° | 13.7 | |
| Washed..... | 5° | 10.8 | |

TABLE II.

*Crystals No. 2 ($A_2$ and $B_2$).*

| Condition of Crystal. | Grazing Angle. | Width at Half-Max. | Per Cent. Reflect. |
|---|---|---|---|
| | Slit $L_3$ between Crystals. | | |
| Split | 3° | 10.6 | 24.8 |
| | 5° | 10.4 | 15.3 |
| | 7° | 8.7 | 13 |
| Surfaces polished and washed | 3° | 10.9 | 22.1 |
| | 5° | 11.5 | 14.7 |
| | 5° | 11.1 | 15.5 |
| | 7° | 10.9 | 11.5 |

These crystals showed so much irregularity in structure, when examined by this method, that but little effect was produced by changing the condition of the reflecting surfaces. In this respect there is a striking contrast between rock-salt and calcite.

The double spectrometer has been applied to crystal reflection by A. H. Compton,[1] and more recently by W. L. Bragg[2] to the investigation of the reflection from imperfect crystals (rock-salt). In this last paper, as an illustration of effect of regular and irregular structure on reflection, Professor Bragg gives two rocking curves. The second crystal in these cases was a thin slab and the curves were taken by transmission. The curve which is given in illustration of regularity of structure is very broad, however. Its breadth is about 30 minutes of arc at half-maximum. This indicates that (*a*) the beam coming from the first crystal to the second was very non-homogeneous, or (*b*) that the second crystal was very irregular in structure, or (*c*) that both of these were true.

Our rocking curves for rock-salt specimens which are manifestly imperfect are more narrow than this one given by Professor Bragg. The experiments previously described for the case of calcite gave rocking curves that are 100 times as narrow as this curve. Calcite approximates to a perfect crystal but is not, of course, completely perfect. This great width of curve given by Professor Bragg would indicate that the crystals were quite imperfect.

Curves Nos. 1, 2 and 3 were all taken with slit $L_3$ in place. *When*

[1] Proc. Am. Phys. Society, PHYS. REV., July, 1917.

[2] Phil. Mag., March and July, 1921.

*slit $L_3$ was removed so that the rays came from a large portion of the crystal surface, these irregularities were washed out.* The curves were regular and smooth, although the crystal was quite imperfect.

It has been noted by a number of experimenters that greater energy is apparently obtained from rock-salt at a first reflection than from calcite. Our results, however, indicate that rock-salt is not so good a reflector as calcite. The calcite *gives a more complete reflection and a much more homogeneous beam of x-rays than rock-salt.* The greater energy observed from rock-salt is due to the fact that at any one position of the crystal the portion ($\Delta\lambda$) selected from the continuous x-ray spectrum is much wider than in the case of calcite.

The results obtained indicate that:

Rock-salt crystals are more apt to be irregular and defective than calcite.

Rock-salt is not so good a reflector of x-rays as calcite.

Rock-salt, owing to irregularities, gives a much less homogeneous beam of x-rays by reflection than calcite.

PHOENIX PHYSICAL LABORATORY,
COLUMBIA UNIVERSITY,
December 6, 1921.

# SOLUBILITY OF $CO_2$ AND $N_2O$ IN CERTAIN SOLVENTS.

BY WILLIAM KUNERTH.

SYNOPSIS.

*Solubility of $CO_2$ and $N_2O$ in Twelve Solvents, 18° to 36° C.*—Since according to the Lewis-Langmuir theory these two gases have similar molecular structures, it is of interest to compare their solubilities in various liquids. In the method adopted, the air was thoroughly removed from the solvent by boiling and then the gas to be tested, having been carefully purified with the help of liquid air, was admitted and shaken up with the solvent until no further solution took place. Observations accurate to better than one per cent. were made for *water, acetone, acetic acid, methyl alcohol, pyridine, ethyl alcohol, benzaldehyde, aniline, amyl acetate, ethylene bromide, isoamyl alcohol, and chloroform.* Taken in this order, the ratio of the solubility of $CO_2$ to that of $N_2O$ decreases regularly from 1.34 (20°) for water to 0.66 for chloroform. This range of variation is small, and moreover the ratio is nearly constant for each solvent, changing less than one per cent. for six solvents, and not more than three per cent. for the others except chloroform and acetone. Also, the temperature coefficient ($ds/sdT$) is in most cases nearly the same for the two gases. It is always negative, the solubility decreasing with increasing temperature.

*Discussion of Suggested Solubility Relations, for Gases in Liquids.—Raoult's law* does not hold for the solubility of gases in liquids. It is also shown that there is little, if any, relation between solubility and the difference between the internal or *cohesion pressures* of solvent and solute. However, the ratio of the solubilities of $CO_2$ and $N_2O$ varies regularly with the *dielectric constant* of the solvent, and since this constant may be taken as an index of the *polarity* of the solvent and since $CO_2$ is more active chemically and therefore has stronger polarity than $N_2O$, this result suggests that polarity may be an important factor in determining the relative solubility of gases in liquids.

## INTRODUCTION.

IN view of the great interest in molecular structure at this time and in view of the possible relation between it and solubility it has seemed of interest and importance to get more complete and more accurate data on certain types of solubility than have hitherto been available.

In the work which is here to be described the solubility of carbon dioxide and of nitrous oxide in twelve different liquids was determined over a range of 18° C. These gases were used because according to recent theories of molecular structure[1] they have the same number and arrangement of electrons. They should therefore exhibit little if any difference in solubility, if the latter depends only on the number and arrangement of electrons. If they do show difference then, according to these theories, it must be due to other properties and the magnitude of the difference should be of interest for any theory of solubility.

[1] Kossell, Ann. der Physik, 49, p. 229 (1916). Lewis, Jour. of Amer. Chem. Soc., 38, p. 762 (1916). Langmuir, Jour. of Amer. Chem. Soc., 41, p. 868 (1919). Thomson, Phil. Mag., 37, p. 419 (1919).

## Apparatus.

The apparatus used for this work was very much like that used by McDaniel.[1] The chief part of it is shown in figure 1. It consists of a gas burette *A* (vol. 120 c.c.) which is graduated to 0.5 c.c. and can be read to 0.1 c.c., and an absorption pipette *B* (vol. 31.3 c.c.) connected by a glass capillary *C*. The whole forms one solid piece of glass and is clamped to a wooden frame (not shown in the figure) which is held in an upright position on an iron rod near the burette. With this rod as a pivot the apparatus can be very thoroughly shaken when solution of the gas in the solvent is to take place in the pipette.

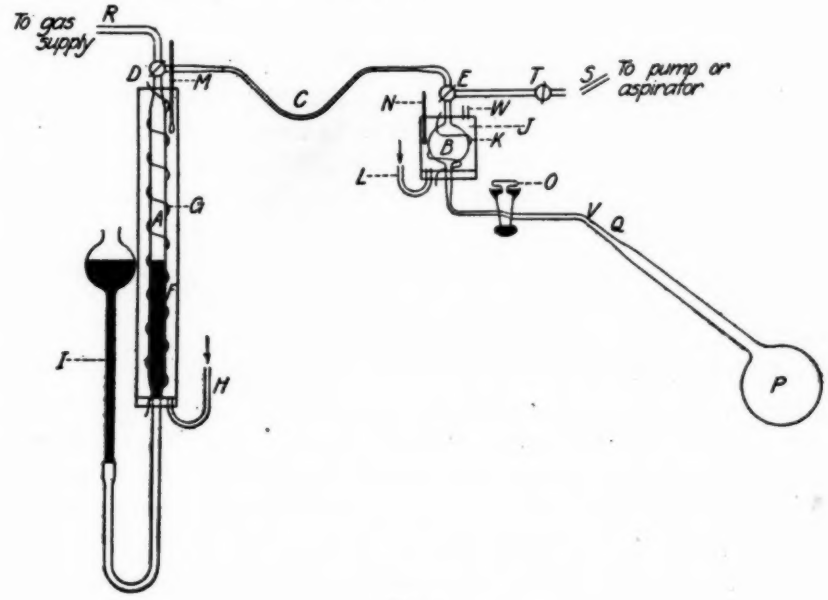



Fig. 1.

At each end of the capillary there is a three-way stopcock (*D*, *E*). The burette is provided with a water jacket *F*, an electric heating coil *G*, and a compressed-air inlet *H*. The reservoir *I* connected with burette *A* by a rubber tube and containing mercury makes it possible to keep the gas in *A* at atmospheric pressure. The pipette is likewise provided with a water jacket *J*, an electric heating coil *K*, and a compressed-air inlet *L*. The coils *G* and *K* are of Chromel *A* wire and either one may be used alone or they may be connected in series. They are so adjusted in length that the resistances are to each other as the respective radiating surfaces of the two water jackets. This insures an equal rate of temperature increase in the two vessels when the coils are in series.

[1] McDaniel, Jour. of Phys. Chem., 15, p. 587 (1911).

Two thermometers *M* and *N* can be read to 0.1° C. and are used to indicate the temperature of the gas in the burette and pipette respectively. *O* is a mercury-seal stopcock, and *P* is a boiler of pyrex glass. *W* is an exit for the air which has been bubbled through the water in *J*. Compressed air is also bubbled through *F* to stir the water and hence assure the same temperature at top and bottom. Stopcock *E* is carefully ground to prevent leakage, and graphite is used as a lubricant on it and also on the mercury-seal stopcock *O*. Grease could be used on neither *E* nor *O* because of the organic solvents used in this work.

## ORDER OF PROCEDURE.

In making any determination the burette *A* is filled with mercury except that a few drops of the solvent to be used are put in at the top. After the air has all been pumped out of the tube *RE* and it has been washed out with the pure gas which is to be used in this work, cock *D* is so adjusted as to allow the pure gas to displace the mercury in the burette. Part of the solvent placed in the burette evaporates and thus saturates the gas with the vapor of the solvent. This arrangement makes it unnecessary, as will appear later, to know the vapor pressure of the solvent at any temperature, a quantity which had to be allowed for in Just's work.[1] It is probably for this reason that Just's results on the solubility of $CO_2$ in liquids do not check very accurately those obtained here. The air is completely removed from the solvent in *P* by boiling for five minutes under reduced pressure and then applying a strong aspirator pump usually for upwards of half an hour more. During this time the solvent in *P* decreases by one fourth or one fifth of its volume. While this is being done *Q* is connected to *S*. Then *Q* is closed by the use of a rubber tube and clip, and forthwith connected to *V*. When the air has next been pumped out of *B* with a good vacuum pump, the boiler *P* is raised above the level of *B* and sufficient air-free solvent is run into *B* by gravity to approximately half fill *B*. To make sure that the last trace of air has been removed from the capillary *C*, this tube is in each case washed out twice with pure gas before a solubility determination is made. A short stub of pressure tubing is used to connect *V* and *Q*. Through this the liquid runs from *P* into *B*. Since this takes only a moment and since the liquids here used have little if any affect on rubber, this proceeding is not objectionable. The solvent is thus at no time exposed to air after once the air has been removed.

The air is then pumped out of the capillary *C* and after stopcock *T* has been closed and *A*, *C*, and *ET* allowed to communicate with each

[1] Just, Z. S. für Phys. Chemie, 37, p. 342 (1901).

other, the height of gas in *A* at atmospheric pressure is carefully read. The mercury reservoir *I* can be raised or lowered to secure atmospheric pressure in *A*. Next *E* is turned so as to bring *B* and *A* into communication, *B* is then shaken to hasten solution and the mercury in *A* rises indicating the volume of gas dissolved. When further shaking causes no more decrease in the volume of the gas in *A* the solution is assumed to be saturated. This takes only a few minutes of thorough agitation of *B*. This apparatus can be shaken more vigorously than that of other investigators and hence solution is hastened. Since the burette is close to the pivot of the apparatus the mercury in it is little agitated when the pipette is vigorously shaken. In consequence of this there was no emulsion between the mercury and the layer of solvent in the burette above the mercury.

Before solution takes place the temperature is made the same in the two jackets *A* and *B* either by the use of ice water or the electric heating coils. After the reading has again been taken on the burette the temperature is raised simultaneously in both burette and pipette by means of coils *G* and *K*. During this time the shaking is continued, and at the proper time readings are repeated on the burette at intervals of 2° up to 36°. At a temperature much below that of the room it is difficult to keep the two jackets constant and at the same temperature because of radiation.

When the reading for the temperature at 36° has been taken the solvent in *B* is measured in a small graduate calibrated to 0.2 c.c. Dividing the volume of gas which disappears into the solvent by the volume of solvent used gives the solubility at any one temperature. In order to determine the solubility at the other temperatures correction for temperature change has to be applied to the volume of the solvent and also for the expansion of the gas when saturated with the vapor of the solvent as it is in burette *A*. The expansion coefficient of the latter is determined separately in the ordinary way either before or after a regular run. Every determination on solubility is repeated at least once, and recorded results are accurate to within about 1 per cent.

The nitrous oxide for this work was obtained from a steel cylinder of the gas purchased from the S. S. White Dental Company. It was rated as 99.7 per cent. pure, and to further insure its purity it was frozen with ethyl alcohol and liquid air, and while it was in that state all the gases were pumped off. When the frozen nitrous oxide had been thus sublimed it was passed over $P_2O_5$ and thus freed from possible traces of moisture. Its density was then determined and found to be 1.968 grams per liter at standard temperature and pressure.

With the exception of a short stub of pressure tubing connecting the steel cylinder with the glass system, the entire apparatus containing the purified gas was one piece of solid glass. This insures the continued purity of the gas when it has once been obtained in pure form, and as it is always under pressure a leak would mean a loss of gas rather than a contamination and would be registered on the attached manometer.

The carbon dioxide was made by heating $NaHCO_3$; and after the gas had passed through a long $CaCl_2$ tube to free it from the water, it was treated in the same way as was the nitrous oxide.

The solvents were obtained from standard chemical companies, and tests for boiling point and density were found to be in accord with the tables.

## RESULTS.

Table I. shows the solubilities of $CO_2$ and of $N_2O$ in each one of the twelve liquids used, at intervals of 2° from 18°–36°. The solubility is expressed in c.c. of the gas under existing barometric pressure and at the temperature specified, per c.c. of solvent under the same conditions. It will be noticed that the solubility decreases as the temperature increases, also that the solubilities of $CO_2$ and of $N_2O$ in any one solvent at a given temperature are very much alike.

Table II. represents the coefficient of temperature change of solubility times $10^2$, *i.e.*, $(ds/s \cdot dt)$ at the temperatures indicated. In each case the solubility decreases with increase of temperature.

In Table III. the second column contains the number of molecules of the solvent ($M_{\text{solvent}}$) for each molecule of $CO_2$ ($M_{CO_2}$) in a saturated solution at 20° C. The last column contains the corresponding number of molecules of solvent for each molecule of $N_2O$.

## ATTEMPTS AT THE PREDICTION OF SOLUBILITY BY RAOULT'S LAW.

There are two general principles which have been used in the endeavor to predict solubility and it will be of interest to see how these fare in the interpretation of the foregoing results.

The first one to use Raoult's Law in an attempt to predict solubility seems to have been Dolezalek.[1] As used by him this law means that the partial vapor pressure of one component divided by its vapor pressure when pure and in the liquid state is equal to its number of molecules divided by the total number of molecules in the solution. It is an empirical law giving, for a very limited number of substances,[2] a linear relationship between concentration and vapor pressure.

[1] Dolezalek, Z. S. für Physik Chemie, 64, p. 727 (1908) and p. 1919 (110).

[2] Dolezalek, Z. S. für Physik Chemie, 64, p. 728 (1908).

TABLE I.

| | Water. | | Acetone. | | Acetic Acid. | | Pyridine. | | Methyl Alcohol. | | Ethyl Alcohol. | | Benzaldehyde. | | Aniline. | | Amyl Acetate. | | Ethylene Bromide. | | Isoamyl Alcohol. | | Chloroform. | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $CO_2$. | $N_2O$. | $CO_2$. | $N_2O$. | $CO_2$. | $N_2O$. | $CO_2$. | $N_2O$. | $CO_2$. | $N_2O$ | $CO_2$. | $N_2O$. | $CO_2$. | $N_2O$. | $CO_2$. | $N_2O$. | $CO_2$. | $N_2O$. | $CO_2$. | $N_2O$. | $CO_2$. | $N_2O$. | $CO_2$. | $N_2O$. |
| 18° | .... | 0.703 | .... | 6.30 | 5.40 | 5.00 | 3.95 | .... | 3.63 | 3.38 | 2.95 | 3.07 | 3.06 | 3.23 | .... | 1.50 | 4.79 | 5.24 | 2.32 | 2.87 | .... | 2.52 | 3.83 | 5.70 |
| 20 | 0.900 | 0.675 | 6.98 | 6.03 | 5.23 | 4.85 | 3.85 | 3.58 | 3.57 | 3.32 | 2.87 | 2.99 | 2.98 | 3.15 | 1.38 | 1.48 | 4.65 | 5.14 | 2.27 | 2.81 | 1.91 | 2.47 | 3.71 | 5.60 |
| 22 | 0.872 | 0.638 | 6.76 | 5.78 | 5.07 | 4.70 | 3.75 | 3.50 | 3.51 | 3.27 | 2.80 | 2.91 | 2.90 | 3.07 | 1.35 | 1.45 | 4.55 | 5.05 | 2.22 | 2.75 | 1.88 | 2.43 | 3.60 | 5.51 |
| 24 | 0.836 | 0.617 | 6.55 | 5.50 | 4.91 | 4.55 | 3.63 | 3.45 | 3.44 | 3.23 | 2.73 | 2.85 | 2.80 | 3.00 | 1.32 | 1.42 | 4.44 | 4.93 | 2.16 | 2.69 | 1.85 | 2.37 | 3.50 | 5.26 |
| 26 | 0.800 | 0.587 | 6.22 | 5.21 | 4.73 | 4.39 | 3.53 | 3.34 | 3.37 | 3.19 | 2.66 | 2.77 | 2.73 | 2.93 | 1.29 | 1.40 | 4.35 | 4.83 | 2.12 | 2.64 | 1.81 | 2.32 | 3.39 | 5.07 |
| 28 | 0.765 | 0.561 | 5.88 | 4.84 | 4.57 | 4.25 | 3.45 | 3.25 | 3.28 | 3.07 | 2.58 | 2.68 | 2.66 | 2.85 | 1.25 | 1.37 | 4.24 | 4.71 | 2.07 | 2.58 | 1.76 | 2.27 | 3.26 | 4.83 |
| 30 | 0.729 | 0.530 | 5.49 | 4.46 | 4.41 | 4.11 | 3.33 | 3.17 | 3.19 | 2.98 | 2.48 | 2.61 | 2.58 | 2.78 | 1.22 | 1.35 | 4.14 | 4.60 | 2.03 | 2.52 | 1.72 | 2.24 | 3.11 | 4.57 |
| 32 | 0.693 | 0.513 | 5.08 | 4.07 | 4.25 | 3.98 | 3.25 | 3.10 | 3.09 | 2.88 | 2.41 | 2.52 | 2.52 | 2.72 | 1.21 | 1.32 | 4.10 | 4.49 | 1.97 | 2.46 | 1.69 | 2.19 | 2.94 | 4.29 |
| 34 | 0.656 | 0.478 | 4.66 | 3.66 | 4.12 | 3.84 | 3.13 | 3.02 | 2.97 | .... | 2.31 | 2.43 | 2.46 | 2.65 | 1.19 | 1.31 | 4.02 | 4.39 | 1.92 | 2.42 | 1.67 | 2.16 | 2.81 | 4.03 |
| 36 | .... | 0.449 | .... | 3.23 | 4.00 | 3.75 | 3.03 | 2.94 | .... | .... | .... | 2.33 | 2.39 | 2.59 | 1.17 | 1.28 | .... | 4.30 | 1.86 | 2.37 | .... | 2.12 | 2.68 | 3.70 |

By assuming that gases are completely miscible in liquids, Dolezalek has, however, attempted to apply this law to the computation of the mol-fraction of a gas which under a given pressure is soluble in various solvents.

TABLE II.

*Temperature Coefficient of Solubility* $\times 10^2$.

| Solvents. | Solutes. | 18°. | 20°. | 22°. | 24°. | 26°. | 28°. | 30°. | 32°. | 34°. | 36°. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Water | $CO_2$ | 1.78 | 1.88 | 2.00 | 2.12 | 2.23 | 2.35 | 2.47 | 2.58 | 2.70 | 2.80 |
| | $N_2O$ | 2.03 | 2.10 | 2.18 | 2.27 | 2.35 | 2.43 | 2.52 | 2.60 | 2.68 | 2.76 |
| Acetone | $CO_2$ | 0.84 | 1.27 | 1.73 | 2.20 | 2.66 | 3.14 | 3.60 | 4.13 | 4.62 | 5.12 |
| | $N_2O$ | 1.50 | 1.96 | 2.44 | 2.94 | 3.42 | 3.93 | 4.40 | 4.92 | 5.40 | 5.90 |
| Acetic acid | $CO_2$ | 1.60 | 1.63 | 1.65 | 1.66 | 1.68 | 1.70 | 1.72 | 1.75 | 1.76 | 1.78 |
| | $N_2O$ | 1.60 | 1.62 | 1.63 | 1.63 | 1.64 | 1.64 | 1.65 | 1.65 | 1.65 | 1.66 |
| Methyl alcohol | $CO_2$ | 0.60 | 0.76 | 0.93 | 1.10 | 1.26 | 1.44 | 1.60 | 1.77 | 1.95 | 2.10 |
| | $N_2O$ | 0.40 | 0.58 | 0.77 | 0.97 | 1.18 | 1.38 | 1.57 | 1.77 | 1.97 | 2.17 |
| Pyridine | $CO_2$ | 1.28 | 1.32 | 1.37 | 1.41 | 1.46 | 1.49 | 1.53 | 1.57 | 1.61 | 1.66 |
| | $N_2O$ | 1.08 | 1.11 | 1.14 | 1.17 | 1.20 | 1.23 | 1.26 | 1.29 | 1.32 | 1.36 |
| Ethyl alcohol | $CO_2$ | 1.16 | 1.23 | 1.32 | 1.40 | 1.48 | 1.57 | 1.67 | 1.74 | 1.84 | 1.90 |
| | $N_2O$ | 1.16 | 1.23 | 1.32 | 1.40 | 1.48 | 1.57 | 1.67 | 1.74 | 1.84 | 1.90 |
| Benzaldehyde | $CO_2$ | 1.32 | 1.33 | 1.34 | 1.34 | 1.35 | 1.36 | 1.37 | 1.38 | 1.39 | 1.39 |
| | $N_2O$ | 1.26 | 1.26 | 1.25 | 1.25 | 1.25 | 1.26 | 1.26 | 1.26 | 1.26 | 1.26 |
| Aniline | $CO_2$ | 1.12 | 1.10 | 1.07 | 1.05 | 1.03 | 1.02 | 1.00 | 0.98 | 0.97 | 0.95 |
| | $N_2O$ | 0.83 | 0.84 | 0.85 | 0.87 | 0.89 | 0.90 | 0.91 | 0.93 | 0.94 | 0.96 |
| Amyl acetate | $CO_2$ | 1.35 | 1.30 | 1.24 | 1.19 | 1.16 | 1.10 | 1.03 | 0.98 | 0.93 | 0.88 |
| | $N_2O$ | 1.03 | 1.04 | 1.05 | 1.06 | 1.07 | 1.09 | 1.10 | 1.11 | 1.12 | 1.13 |
| Ethylene bromide | $CO_2$ | 1.07 | 1.10 | 1.13 | 1.16 | 1.18 | 1.21 | 1.24 | 1.26 | 1.29 | 1.32 |
| | $N_2O$ | 1.06 | 1.06 | 1.07 | 1.08 | 1.09 | 1.10 | 1.11 | 1.12 | 1.13 | 1.14 |
| Isoamyl alcohol | $CO_2$ | 1.00 | 0.98 | 0.97 | 0.96 | 0.96 | 0.95 | 0.95 | 0.94 | 0.94 | 0.93 |
| | $N_2O$ | 1.00 | 0.98 | 0.97 | 0.96 | 0.96 | 0.95 | 0.95 | 0.94 | 0.94 | 0.93 |
| Chloroform | $CO_2$ | 1.10 | 1.30 | 1.53 | 1.77 | 2.00 | 2.20 | 2.43 | 2.66 | 2.90 | 3.10 |
| | $N_2O$ | 0.66 | 1.03 | 1.40 | 1.80 | 2.20 | 2.58 | 2.98 | 3.35 | 3.70 | 4.07 |

If Dolezalek's assumption of the validity of Raoult's Law, thus defined, for mixtures of gases in liquids is correct, then obviously the solubility of gases in liquids can be completely predicted if we mean by solubility[1] the mol-fraction of one substance which will be mixed with the other under a given condition of temperature and external pressure. In Dolezalek's paper in which he attempts to test this assumption, he obtains results which are in accord with the theory. However, when the same method is applied to other data wide deviations are found even with the constant he uses.

To see how well we fare in this work in predicting solubilities of gases in liquids by the use of Raoult's Law, let us turn to the first two columns

[1] This use of the word "solubility" is somewhat confusing since it differs from the usual acceptation of the term. This confusion might be reduced by replacing the word "solubility" in its ordinary usage by the word "miscibility."

TABLE III.

| | $M_{solvent}$ $M_{CO_2}$. | $M_{solvent}$ $M_{N_2O}$. |
|---|---|---|
| Water | 1350 | 1800 |
| Acetone | 46 | 53 |
| Acetic acid | 73 | 79 |
| Methyl alcohol | 155 | 167 |
| Pyridine | 72 | 77 |
| Ethyl alcohol | 131 | 126 |
| Benzaldehyde | 73 | 69 |
| Aniline | 174 | 162 |
| Amyl acetate | 32 | 29 |
| Ethylene bromide | 111 | 90 |
| Isoamyl alcohol | 106 | 82 |
| Chloroform | 74 | 49 |

in Table IV. Here are shown the solubilities of $CO_2$ and of $N_2O$ in terms of mol-fractions in the twelve different solvents used. In the first column of Table V. are shown the solubilities of $CO_2$ in terms of mol-fractions in twenty different solvents as found by Just. For $CO_2$ under ordinary conditions the mol-fraction according to Raoult's Law would be 0.0178 = (1/56.3 atm.). This should be the same for all

TABLE IV.

| Solvents. | Solubility in Mol-fractions $\times 10^4$ at 20°. | | Internal Pressures at 0° C. in Atmospheres. | | |
|---|---|---|---|---|---|
| | $CO_2$. | $N_2O$. | *A.* | *B.* | *C.* |
| Amyl acetate | 283 | 312 | 1,500 | — | — |
| Acetone | 211 | 185 | 2,230 | 2,600 | 4,440 |
| Pyridine | 129 | 120 | 2,460 | — | — |
| Benzaldehyde | 125 | 134 | 2,440 | — | — |
| Acetic acid | 124 | 115 | 2,100 | 5,960 | 7,140 |
| Chloroform | 121 | 182 | 2,030 | 2,430 | 3,030 |
| Isoamyl alcohol | 87 | 111 | 2,400 | — | — |
| Ethylene bromide | 82 | 100 | 2,200 | 1,980 | 4,400 |
| Ethyl alcohol | 69 | 72 | 3,720 | 3,760 | 3,120 |
| Methyl alcohol | 60 | 53 | 4,730 | 6,360 | 4,030 |
| Aniline | 53 | 56 | 2,740 | 3,300 | — |
| Water | 7 | 5 | 11,600 | 17,300 | — |
| $CO_2$ | | | 985 | 1,510 | — |
| $N_2O$ | | | 980 | 1,440 | — |

solvents. From Tables IV. and V. here given we see that the mol-fractions are not what this theory predicts at all and that they are by no means alike. Thus it becomes apparent that this law rarely, if ever, holds for gases dissolved in liquids. This is in accord with the conclusion arrived at by Hildebrand.[1] It means that the procedure of Dolezalek is utterly worthless for predicting solubility of gases in liquids.

TABLE V.

| Solvents. | Solubility of $CO_2$ in Mol-fractions $\times 10^4$ at 20°. | Internal Pressures at 0° C. in Atmospheres. | | |
|---|---|---|---|---|
| | | *A.* | *B.* | *C.* |
| Amyl acetate | 270 | 1,500 | — | — |
| Acetone | 209 | 2,230 | 2,600 | 4,440 |
| Pyridine | 129 | 2,460 | — | — |
| Benzaldehyde | 128 | 2,440 | — | — |
| Ethylene chloride | 125 | 2,070 | 2,730 | 4,500 |
| Chloroform | 123 | 2,030 | 2,430 | 3,030 |
| Acetic acid | 121 | 2,100 | 5,960 | 7,140 |
| Nitrobenzene | 113 | 2,340 | — | — |
| Toluene | 107 | 1,710 | 2,210 | 3,570 |
| Meta xylene | 102 | 1,670 | 2,100 | — |
| Carbon tetrachloride | 100 | 1,685 | 2,030 | 3,220 |
| Benzene | 91 | 1,870 | 2,240 | 3,900 |
| Ethylene bromide | 82 | 2,200 | 1,980 | 4,400 |
| Propyl alcohol | 77 | 2,970 | 3,020 | 2,480 |
| Methyl alcohol | 71 | 4,730 | 6,360 | 4,030 |
| Ethyl alcohol | 70 | 3,720 | 3,760 | 3,120 |
| O — toluidine | 66 | 2,280 | — | — |
| Aniline | 55 | 2,740 | 3,300 | — |
| Carbon disulphide | 22 | 3,000 | 3,220 | 3,800 |
| Water | 7 | 11,600 | 17,300 | — |

## ATTEMPTS AT THE PREDICTION OF SOLUBILITY FROM COHESION PRESSURES.

The real problem of predicting solubility comes where the components are not completely miscible. The method here to be discussed has been used by Traube,[2] Walden,[2] Hildebrand,[2] and Bradford,[2] and consists essentially in the assumption that two substances will be more nearly soluble in one another in proportion as the internal pressures (Laplace's cohesion constants) of the two substances approach one another. The fundamental idea underlying this theory appears to be that if two

[1] Hildebrand, Jour. of Amer. Chem. Soc., 38, p. 1454 (1916).

[2] Traube, Verh. der d. Physik Gesell, 10, p. 880 (1908). Walden, Z. S. fur Phys. Chemie, 66, p. 409 (1909). Hildebrand, Jour. of Amer. Chem. Soc., 38, p. 1452 (1916). Bradford, Phil. Mag., 38, p. 696 (1919).

substances $A$ and $B$ have the same cohesion pressures when in the liquid state, then the molecules of substance $A$ will exert the same sort of forces upon the molecules of substance $B$ as the molecules of $A$ (or of $B$) exert upon one another. In other words, if $A$'s molecules have a certain attraction for one another as measured by cohesion pressure and $B$'s molecules have the same attraction, then the two substances will readily mix, but if the cohesion pressure of either one is greater than that of the other then the one will draw itself away from the other just as would be expected if there were no such thing as selectivity among molecular forces. This idea is perhaps most definitely expressed in an equation set up by Bradford and written in the form

$$f = \frac{M_A^2}{r_A^4} - \frac{2M_AM_B}{r_{AB}^4} + \frac{M_B^2}{r_B^4} .$$

The $f$ in this expression is what he calls the force opposing solution, the term $M_A^2/r_A^4$ is the term which in his theory is proportional to the internal pressure of substance $A$, whereas the term $M_B^2/r_B^4$ is proportional to the internal pressure of substance $B$. The attraction between molecules of substance $A$ is assumed to be electrical in origin and the term $M$ in Bradford's theory is what he calls the electrical "moments of the atomic doublets in each molecule." He assumes, following the proofs given by J. J. Thomson[1] and by Sutherland,[2] that with such forces the molecular attraction will be inversely proportional to the fourth power of the distance between molecules. Hence he gets the form of the cohesion term $M^2/r^4$. The force drawing molecules $A$ and $B$ together is then of the form $2M_AM_B/r_{AB}^4$, so that the force opposing solution is the difference between this term and the sum of the other two terms which express the cohesion of the molecules for each other respectively.

From this point of view we should be able to calculate the value of the solubility of one component in another if we have given their internal pressures. These I have calculated by three different methods and listed under headings $A$, $B$, and $C$ in Tables IV. and V. for the solvents found in column one in each case. Under $A$ are found the internal pressures obtained by Stefan's method,[3] under $B$ the Laplacian cohesion constant obtained from the expression $K = a(v_1/v_2)^2$, and under $C$ are the internal pressures obtained by use of the expression[4] $K = \alpha T/\beta$ where $\alpha$ is the expansion and $\beta$ the compressibility coefficient. The data required for the calculation of internal pressures were obtained from the Landolt-Börnstein Tables.

[1] Thomson, Phil. Mag., 27, p. 757 (1914).
[2] Sutherland, Phil. Mag. (5), 39, p. 1 (1895).
[3] Stefan, Wied. Ann., 29, p. 655 (1886).
[4] Kleeman, Kinetic Theory of Gases and Liquids, p. 71.

To show how the theory of internal pressures works out when applied to the data here obtained we need to refer again to Table IV. where the solvents are arranged in decreasing order of the solubility of $CO_2$, but the order would be very nearly the same if arranged according to $N_2O$. The cohesion pressure theory requires that the solubility should decrease as the difference of internal pressures between solvent and solute increases. The fact that the solubilities are those at 20° C. and the internal pressures are at 0° C., makes little if any difference in the relative order of solvent and internal pressure. It will be evident from Table IV. that there is no correlation there which is sufficiently good even as evidence that this theory is in its main features correct. It will also be noticed that as far as the reliability of the theory is concerned it is immaterial which of the three methods of calculating internal pressures is used. It is true that some of the solvents are probably associated. But the situation is not improved even by omitting entirely those solvents which we feel confident are associated.

Bradford has used this method for the prediction of solubility with some apparent success, as is shown in the table he cites. But the agreement which is there shown is accidental, I think, and due to the relatively few cases chosen.

Hildebrand [1] also sets up a similar table and draws the conclusion that Bradford does. In my opinion a critical study of his table yields no evidence which justifies a conclusion of this kind, and when this table is extended to more solvents as is done in Table V. above, where the solubilities are those by Just on $CO_2$ and are listed in decreasing order of magnitude, the conclusion Hildebrand draws is very obviously not warranted. When a comparison is made with the theory the departures will be seen to be just as great as in Table IV. So far, therefore, as these data are concerned, this method must be considered practically useless.

Again it should follow from the point of view of this theory that:

1. Substances which have the same internal pressures should all be completely miscible.

2. All substances which are completely miscible should have the same internal pressures.

3. The order of miscibility should be the order of difference in internal pressures.

As to the third point we note from the tables given above that it does not hold at all.

Under the second point should be mentioned many combinations of

[1] Hildebrand, Jour. of Amer. Chem. Soc., 38, p. 1467 (1916).

non-associated liquids miscible in all proportions, the internal pressures of whose components are widely different. These are not in accordance with the theory. Among these may be mentioned ether and benzaldehyde, ether and chloroform, ethylene bromide and ether, ethylene chloride and ether, carbon disulphide and ether. According to the theory these should not be completely miscible. It should be said that Hildebrand also recognizes a difficulty of this sort.

Under the first point above mentioned there are only a few cases to be considered because very few substances have the same or very nearly the same internal pressure. The combinations cited by Hildebrand should be noted. They are benzene and carbon tetrachloride, benzene and chlorobenzene, benzene and chloroform, benzene and ethylene chloride, chlorobenzene and toluene. They have nearly equal internal pressures and are miscible in all proportions. But methyl alcohol should be completely miscible in carbon disulphide, for according to one method at least their internal pressures are nearly alike. The polarity of methyl alcohol is given as the cause of this discrepancy. This suggests that polarity as a factor in solubility may be worthy of further study. But the conclusion of the studies in this field would appear to be that present theories of miscibility, though perhaps of some little value as indices, can scarcely be said to have gained any very notable successes.

## Polarity.

If we now turn to Table VI. where are listed the ratios of solubilities of $CO_2$ to $N_2O$ in the twelve solvents here used, it seems worthy

### Table VI.

*Ratio of Solubility of $CO_2$ to that of $N_2O$.*

| Solvents. | 18°. | 20°. | 22°. | 24°. | 26°. | 28°. | 30°. | 32°. | 34°. | 36°. |
|---|---|---|---|---|---|---|---|---|---|---|
| Water | .... | 1.333 | 1.366 | 1.354 | 1.363 | 1.364 | 1.372 | 1.350 | 1.370 | .... |
| Acetone | .... | 1.157 | 1.170 | 1.191 | 1.194 | 1.215 | 1.230 | 1.248 | 1.272 | .... |
| Acetic acid | 1.080 | 1.078 | 1.078 | 1.078 | 1.076 | 1.075 | 1.072 | 1.067 | 1.072 | 1.066 |
| Methyl alcohol | 1.073 | 1.075 | 1.073 | 1.065 | 1.056 | 1.068 | 1.070 | 1.072 | .... | .... |
| Pyridine | .... | 1.075 | 1.070 | 1.052 | 1.057 | 1.060 | 1.050 | 1.048 | 1.035 | 1.030 |
| Ethyl alcohol | 0.961 | 0.960 | 0.963 | 0.958 | 0.960 | 0.963 | 0.950 | 0.957 | 0.950 | .... |
| Benzaldehyde | 0.048 | 0.946 | 0.945 | 0.933 | 0.932 | 0.933 | 0.928 | 0.927 | 0.928 | 0.923 |
| Aniline | .... | 0.932 | 0.931 | 0.930 | 0.922 | 0.912 | 0.904 | 0.917 | 0.908 | 0.914 |
| Amyl acetate | 0.914 | 0.905 | 0.902 | 0.902 | 0.900 | 0.901 | 0.901 | 0.913 | 0.916 | .... |
| Ethylene bromide | 0.808 | 0.807 | 0.807 | 0.803 | 0.803 | 0.803 | 0.805 | 0.801 | 0.793 | 0.785 |
| Isoamyl alcohol | .... | 0.773 | 0.774 | 0.781 | 0.780 | 0.776 | 0.768 | 0.772 | 0.773 | .... |
| Chloroform | 0.672 | 0.663 | 0.653 | 0.666 | 0.668 | 0.674 | 0.680 | 0.685 | 0.697 | 0.724 |

of note that $CO_2$, which is considered more polar than $N_2O$, is also in general more soluble than $N_2O$ in the solvents considered polar, namely: water, acetone, acetic acid, methyl and ethyl alcohol. $CO_2$ and $N_2O$ are so completely alike in so many ways that it is perhaps difficult to differentiate them on the basis of polarity. The dielectric constant which is usually considered a criterion of polarity is the same in the two cases, but chemical reactivity is also a sign of polarity and in this respect $CO_2$ differs from $N_2O$, being more active than the latter. For the solvents here mentioned we can apply the criterion of the dielectric constant and order their polarities on the basis of this property.

At present there exists little definite quantitative data on the effect of polar substances upon each other and upon non-polar substances in their neighborhood; but so far as the present table goes its indications are that the solubility of gases in liquids is connected with polarity rather than with Raoult's law or with internal pressures.

The indications of the present work then are that the most hopeful lines of attack for the problem of the prediction of solubility must be looked for in the study of chemical properties rather than of physical properties such as internal pressures.

In conclusion the writer wishes to acknowledge his indebtedness to Prof. R. A. Millikan for suggesting the subject, for his kindly interest in this work, and for his continuous friendly advice and help, and to Prof. A. J. Dempster for occasional assistance.

RYERSON PHYSICAL LABORATORY,
CHICAGO, ILL.,
September -, 1921.

# PROCEEDINGS

OF THE

# AMERICAN PHYSICAL SOCIETY.

## MINUTES OF THE NEW YORK MEETING, FEBRUARY 25, 1922.

THE 113th meeting of The American Physical Society was held in the lecture theater of Schermerhorn Hall, Columbia University, New York City, on Saturday, February 25, 1922. There were morning and afternoon sessions with an attendance of about one hundred and seventy-five members and visitors. The president of the Society, Theodore Lyman, presided at both sessions.

There was a meeting of the Council on the evening of Friday, February 24, 1922, at the Columbia University Club. The following elections were made: *elected to Fellowship*, Worth Huff Rodebush; *transferred from Membership to Fellowship*, Walter F. Colby and Orin F. Tugman; *elected to Membership*, William C. Beller, William B. Bohanon, G. Breit, August Concilio, James Cork, Chester S. Cutshall, Pasquale J. Federico, H. C. Frank, W. H. Fulweiler, Elmer Hutchisson, Albert Kalin, Elizabeth A. Mitchell, Pierre LeCompte du Nouy, Chas. W. Prine, J. Howard Rowan, George W. Schneider, George W. Sherman, Jr., Khimji B. Thakkur, J. R. Tolmie, Dare Abernathy Wells, William R. Westhafer and P. B. Winn.

The following program of twenty-eight papers was presented, three, Nos. 3, 5, and 9, being read by title:

1. The Rigidity and Viscosity of Ice. C. D. HAIGIS, presented by A. W. Duff.

2. The Measurement of Intravenous Temperatures. HARRY CLARK.

3. The Effect of Nascent Hydrogen on Hard Steel Magnets. JOHN COULSON.

4. Magnetostriction with Small Magnetizing Fields. JOHN R. HOBBIE, JR.

5. Some Optical and Electrical Properties of Rochelle Salt. J. VALASEK.

6. The Spectrum of Fluorine. HENRY G. GALE.

7. Improvement in the Determination of the Radium Content of Low-Grade Radium Barium Salts. VICTOR F. HESS and ELIZABETH E. DAMON.

8. On the Operating Characteristics of the Audion. LYNDE P. WHEELER.

9. The Effect of Crystal Structure upon Photoelectrical Sensitivity. W. W. COBLENTZ.

10. New Evidence Regarding the Interpretation of Critical Potentials in Hydrogen. P. S. OLMSTEAD.

11. Low Voltage Arcs in Diatomic Gases and the Effect of Dissociation in a Tungsten Furnace. O. S. DUFFENDACK, introduced by K. T. Compton.

12. Magnetic Control of Thermionic Emission from a Straight Wire by Current in the Wire. ALBERT W. HULL.

13. A Test of Theories of Cumulative Ionization. K. T. COMPTON.

14. The Scattering of Electrons by Aluminum. C. DAVISSON and C. H. KUNSMAN.

15. The Ratio of the Two Elementary Charges. F. W. LOOMIS.

16. Ionization and Radiation Potentials and the Size of the Atom. BERGEN DAVIS.

17. On the Spectra of X-Rays of Short Wave-Lengths. WILLIAM DUANE and K. C. MAZUMDER.

18. The Crystal Structure of Silver-Palladium and Silver-Gold Alloys. L. W. MCKEEHAN.

19. Precision Measurement of Crystals. WHEELER P. DAVEY.

20. A Spectrographic Study of Ultraviolet Fluorescence Excited by X-Rays. J. O. PERRINE.

21. The Grating Space of Mica and the Intensities of the Spectral Orders. BERGEN DAVIS and H. M. TERRILL.

22. A New Type of Bumstead Electrometer and Accessory Apparatus. HARRY CLARK.

23. Dynamic Characteristics of Helium Arcs. FABIAN M. KANNENSTINE.

24. The Joule Effect in Steel Rods at Different Drawing Temperatures. S. R. WILLIAMS and O. KOPPIUS.

25. Effects Obtained with an Alternating Current Sent Through a Capillary Electrometer. R. D. KLEEMAN and D. T. SIMMONDS.

26. Note on the Formation of Negative Ions in a Gas. R. D. KLEEMAN.

27. Note on X-Ray Spectra. WILLIAM DUANE and R. A. PATTERSON.

28. The Electric Fields of Some Constant Electromagnetic Systems in Motion. S. J. BARNETT.

The abstracts of the papers in the above program, with corresponding numbers, are given on the following pages.

DAYTON C. MILLER,
*Secretary.*

## 1. THE VISCOSITY AND RIGIDITY OF ICE.

BY C. D. HARGIS.

PREVIOUS work, principally by Hess in 1902, showed that the coefficient of viscosity of ice increases with the time that the shearing stress has been acting. He found for the coefficient a value of $.6 \times 10^{11}$ after 15 seconds and a value of $120 \times 10^{11}$ after 28,000 seconds. Using these results he showed that the slow motion of a glacier can be accounted for.

In the present work the coefficient of viscosity and the rigidity were determined kinetically under conditions where the time of shear was a fraction

of a second. A cylinder of ice was frozen in a brass tube, withdrawn, and mounted as a torsional pendulum, the upper end being frozen solidly to a support. The lower end was free and carried a mass whose moment of inertia was $5.67 \times 10^5$ gm. cm.$^2$ and in addition a small mirror. A ray of light from an arc light was reflected by the mirror through lenses onto a moving film which also had seconds intervals recorded by a small filament flashing at intervals of a second. The equation giving the motion of the rod is of the form

$$K \frac{d^2\theta}{dt^2} + L \frac{d\theta}{dt} + M\theta = 0,$$

where

$$L = \eta \frac{\pi r^4}{2L} \qquad \text{and} \qquad M = n \frac{\pi r^4}{2L}.$$

This equation integrated gives the coefficient of viscosity and the rigidity in terms of the logarithmic decrement, period, length, radius, and moment of inertia.

A pendulum 226 cm. in length, of period .468 second and radius .863 cm. gave for the coefficient of viscosity $6.12 \times 10^9$ and for the rigidity $2.66 \times 10^{10}$. Another pendulum of length 111 cm., period .286 second and radius .802 cm. gave for the coefficient of viscosity $3.8 \times 10^9$ and for the rigidity a value of $2.91 \times 10^{10}$. The average value of the rigidity from eight observations was $2.82 \times 10^{10}$ and the coefficient of viscosity varied from $3.8 \times 10^9$ for a period of .286 second to $6.33 \times 10^9$ for a period of .448 second. The mean deviation of the eight observations of rigidity from the value $2.82 \times 10^{10}$ was $.15 \times 10^{10}$.

WORCESTER POLYTECHNIC INSTITUTE.

## 2. THE MEASUREMENT OF INTRAVENOUS TEMPERATURES.

BY HARRY CLARK.

A COPPER-CONSTANTAN thermocouple is sealed inside a steel tube, which is small enough in diameter to pass freely through a hypodermic needle. It can thus be placed in a blood vessel, the flow of blood between the tube and the needle showing when the vessel has been properly located. Temperatures are read by a galvanometer-deflection method. The second thermal junction is kept at $37 \pm 0.001°$ C. by means of an electrical thermostat which operates without stirring device or relay, and from which the troubles caused by fouling of the mercury contact have been entirely eliminated. Experiments on animals show that the blood temperature remains constant to within perhaps 0.01° C. over considerable lengths of time. Clinical experiments will be begun shortly to determine the degree of importance to be attached to such measurements.

THE ROCKEFELLER INSTITUTE OF MEDICAL RESEARCH,
NEW YORK CITY.

## 3. The Effect of Nascent Hydrogen on Hard Steel Magnets.

By John Coulson.

Investigations having proven that steel absorbs hydrogen at ordinary temperatures it was considered probable that the "aging" of *permanent magnets* was due primarily to the action of slowly absorbed hydrogen. Bar magnets of "Special Alloy Magnet Steel" and high carbon steels were exposed to the action of electrolytic hydrogen while serving as kathode in an electrolyte of 25 per cent. $H_2SO_4$. Results of observation are given in table and in curves showing the decrease in magnetic moment as a function of the time of exposure.

Well *seasoned* magnets of drill rod, quenched glass-hard, underwent a further decrease in moment of 14 per cent. on exposure to the hydrogen. The moment of similar magnets of spring steel and special magnet steel experienced a precipitous drop in the course of the electrolytic treatment, which was not in evidence with magnets of drill rod. For magnets of spring steel this sudden drop occurred after 20 or 30 minutes' exposure, and amounted to about 5 per cent. For the special magnet steel it occurred after a few minutes, and in some cases had a magnitude of 19 per cent. Before and after this sudden transition the rate of change in moment was only a fraction of one per cent.

Exposing the magnets to the electrolytically evolved hydrogen in heated electrolyte accelerated this aging process. At 60° C. the magnetic moment reached stability in an hour or less. Hammering the magnet at this stage had little or no effect on its moment. The effect usually is about one part in 1600.

Photographs of cold-rolled steel broken under stress show the depth to which the electrolytic hydrogen penetrated for 40 seconds' exposure.

University of Pittsburgh.

## 4. Magnetostriction with Small Magnetizing Fields.

By John R. Hobbie, Jr.

*Piezo-electric Method of Measuring Extremely Small Magnetostriction Effects.*—In this method, suggested by Pupin, the wire to be studied is surrounded by a solenoid through which an alternating current of known strength and frequency is sent, and the vibrations set up in the wire are transmitted to a piezo-electric crystal and the resulting electric charge is amplified and measured.

For elongations down to $2 \times 10^{-9}$ the wire was hung directly from a *quartz crystal.* To measure the charge produced by a given magnetizing current, an electromotive force of the same frequency, and adjusted to the proper phase by means of a *Pupin wave balance*, was fed to the amplifier through a vacuum tube in parallel with the one connected to the crystal, and the potential was varied until the note produced by the crystal was balanced out. The force corresponding to a given charge was determined with the aid of a condenser, one plate of which was suspended from the crystal.

By using the torsion of a *Rochelle salt crystal* the sensitiveness of the method was extended to $2 \times 10^{-11}$, and by tuning both the crystal and wire to resonance

with the frequency used, a sensitiveness of $3 \times 10^{-12}$ was reached. The last two arrangements were calibrated in absolute units by comparison of the results with those obtained with quartz. The smallest change previously measured was about $10^{-8}$.

*Magnetostriction with Small Magnetizing Fields.*—An *iron* wire and a *nickel* wire were studied. In each case the curve for magnetostriction as a function of the field is nearly linear, but slightly concave downward in its lower portion, and apparently passes through the origin. For fields of 1, 0.05 and 0.002 gauss, the ratio of magnetostriction to field strength is respectively 3, 2.4 and $4 \times 10^{-9}$ for iron, and 2, 1 and $3 \times 10^{-9}$ for nickel. The *probable* error is from 7 to 10 per cent.

COLUMBIA UNIVERSITY.

## 5. SOME OPTICAL AND ELECTRICAL PROPERTIES OF ROCHELLE SALT.

BY J. VALASEK.

THE three main indices of Rochelle salt have been measured for several wave-lengths in the visible region and for temperatures between $-70°$ C. and $+40°$ C. Their variation with temperature was approximately linear throughout the range although the dielectric and piezoelectric constants both undergo an increase of several hundred per cent. in the temperature interval of $-25°$ to $-15°$ C. and a corresponding decrease in the interval of $+20°$ to $+30°$ C. Hence the doublets responsible for the large piezoelectric and dielectric action of Rochelle salt have a low natural frequency somewhere well below the immediate infra-red.

In order to ascertain whether the large temperature coefficient of the indices of refraction was, as usual, due to a changing density, the coefficients of expansion were measured in the three main directions by the Fizeau method. On applying the Lorentz-Lorentz formula,

$$\frac{n^2 - 1}{n^2 - \frac{\alpha - 1}{\alpha}} = \alpha C\rho,$$

the above view was confirmed but the values of $\alpha$ necessary to fit the observations were much smaller than the value of 1/3 for a uniform distribution of charges. The values differed for the three indices but were always between zero and one-tenth. In general a small $\alpha$ means that the force on the charges which have an appreciable effect in dispersion is nearly equal to the electric vector of the incident wave and hence a formula of the Sellmeier type should represent the dispersion.

Preliminary observations indicate the existence of a "real" pyroelectric effect in Rochelle salt. Below 0° C. the natural polarization of the crystal increases and causes a charge to appear on the faces of a plate cut normal to the ă axis when it is heated. Above 0° C. the opposite variation of charge

takes place. Since the dilatations are monotonically increasing while the pyroelectric charge reverses in sign, there is evidence here of a real pyroelectric effect the existence of which is doubted by Voigt from observations made on other crystals.

UNIVERSITY OF MINNESOTA,
February 8, 1922.

## 6. THE SPECTRUM OF FLUORINE.

BY HENRY G. GALE.

FLUORINE has been generated with the apparatus described by Smythe (Astrophysical Journal, 44, 133, 1921). Heavy copper electrodes tipped with gold, were inserted through ground joints into a bulb of about 500 c.c. capacity, and the spectrum photographed through a fluorite window at atmospheric pressure. The spectrum has also been photographed at reduced pressures, using an ordinary vacuum tube with copper electrodes. A concave grating of 1.5 meters' radius was used, the ruled surface, 10 cm. by 4 cm., having 600 lines per mm. The lines are of fair quality at atmospheric pressure, and are very sharp at a pressure of about 6 mm. to 10 mm. Measurements have been made on 52 lines between $\lambda$ 3470 and $\lambda$ 7800. Except 7 lines to the red of $\lambda$ 7400, all of these are included in the tables of Exner and Haschek, Porlezza, Lunt or Moissan. With a powerful spark, 15 additional lines appear in the red and orange regions. The wave-lengths are accurate to about .05 Å. There are a number of interesting triplets and doublets.

UNIVERSITY OF CHICAGO.

## 7. IMPROVEMENT IN THE DETERMINATION OF THE RADIUM CONTENT OF LOW-GRADE RADIUM BARIUM SALTS.

BY VICTOR F. HESS AND ELIZABETH E. DAMON.

THE present gamma-ray methods of determining the radium content of low-grade radium salts are rather inaccurate due to the varying influence of the absorption of the salt itself. Likewise the emanation method gives a lesser degree of accuracy because repeated dilutions of the liquid are necessary.

One of the authors has devised a portable string electrometer (electric capacity 1 cm.) which is very sensitive. A hollow curved tin plate container (10 cm. high, 2 cm. thick) was filled with inactive barium salts and placed at a distance of 30 cm. (the radius of curvature of the tin plate container) from the center of the electrometer. A small radium tube (0.87 mg.) was imbedded in the salt at different positions throughout and the average of these readings agreed with the average of two readings taken with the radium tube fixed on the outside wall of the container, front and back, within one per cent.

The container was then filled with another salt, but radioactive. Readings were taken with and without the standard attached and the amount of radium computed. Knowing the quantity of salt in the container results may be

expressed in mg. of radium per kg. Equilibrium values may be calculated from two successive readings.

A concrete example may illustrate: a sample dissolved in hydrochloric acid and residues decomposed again gave, measured by the emanation method, 1.05 mg. Ra/kg. Sample of the same material dissolved in concentrated sulfuric acid gave 1.11 mg./kg. (emanation method). The gamma-ray method described above gave 1.10 mg./kg. This method has the advantage of greater accuracy and requires much less time.

U. S. RADIUM CORPORATION, ORANGE, N. J.

## 8. ON THE OPERATING CHARACTERISTICS OF THE AUDION.

BY LYNDE P. WHEELER.

IN order to predetermine the behavior of the three-element thermionic vacuum tube when functioning in a given circuit, it is important to have a grid voltage-plate current characteristic for the operating conditions. Such curves are usually obtained experimentally for each value of the contemplated impedance of the plate circuit.

It is shown in this paper how these operating characteristics can be computed from the ordinary static characteristics of the tube which are measured with negligible impedance in the plate circuit. Only the case where the external impedance is a pure resistance is treated. The extension of the results to include reactance can be readily made.

The expression by means of which such computations can be made is obtained by transforming the parabolic equation for the plate current in terms of the grid and plate voltages into one in terms of the external and internal resistances of the plate circuit. When this is accomplished, it appears that the operating characteristic can be obtained from the simple static characteristic of the tube without external resistance by multiplying each ordinate of the latter by a numerical factor whose magnitude depends only on the ratio of the external and internal resistances. This factor is a constant for a steady, and very approximately so for an A.C., e.m.f. applied in the grid circuit. Its magnitude varies from unity when the external resistance is zero to zero when it is infinite.

It is further shown how an expression for the A.C. component of the plate current can be obtained when the characteristic is parabolic. From the form of this expression it is seen that in addition to producing distortion, the curvature of the characteristic changes the effective resistance of the plate circuit from that which obtains for a linear characteristic. The factor which determines the magnitude of this change also depends only on the ratio of the external and internal resistances, and varies from unity when the external resistance is zero to two when it is infinite. Thus the common statement that the effect of curvature is to introduce harmonics but not to change the magnitude of the fundamental component of the plate current must be modified.

YALE UNIVERSITY.

## 9. The Effect of Crystal Structure upon Photoelectrical Sensitivity.

By W. W. Coblentz.

Silver sulphide, $Ag_2S$, as a mineral, occurs in two crystal forms: *Argentite* which is isometric and *Acanthite* which is orthorhombic. Both minerals are photoelectrically sensitive, and hence form interesting material for studying the effect of crystal structure upon photosensitivity.

*Argentite.*—Applying spectral radiation stimuli of equal energy, it is found that, at 20° C., argentite reacts slightly to radiations of wave lengths 0.6 $\mu$ to 1.1 $\mu$, followed by a sharp, fairly symmetrical maximum at 1.35 $\mu$. At low temperatures (− 100° C.) this maximum shifts to the short wave-lengths, − 1.1 $\mu$. At all temperatures the spectrophotoelectrical reaction appears to be positive, *i.e.*, the resistance decreases when the mineral is exposed to radiation. The general outline of the curve exhibiting the spectrophotoelectrical reaction is fairly uniform for different samples.

*Acanthite.*—The electrical reaction of acanthite differs from that of argentite in that the radiation stimulus appears to induce a photo-negative response (increase in resistance, or counter e.m.f.) which is superposed upon the photo-positive response usually observed in substances exhibiting photosensitivity. Moreover, at 20° C. the photoelectrical reaction is high for radiations of wave-lengths 0.6 $\mu$ to 1.1 $\mu$, followed by an unsymmetrical maximum at 1.4 $\mu$. At low temperatures the sensitivity curve is symmetrical with the maximum shifted to 1.2 $\mu$. The general outline of the curve exhibiting the spectro-photoelectrical reaction differs greatly for different samples. Since the samples examined are usually aggregates of crystals, which are no doubt irregularly arranged, it would appear that, in the orthorhombic crystal, the inequality of the axes has a marked effect upon spectro-photoelectrical conduction.

Washington, D. C.,
February 4, 1922.

## 10. New Evidence Regarding the Interpretation of Critical Potentials in Hydrogen.

By P. S. Olmstead.

*Method of Producing Atomic Hydrogen.*—A close grid of tungsten wires was introduced close to the gauze in an ionization tube of the Lenard type. By heating this grid to incandescence, a certain amount of atomic hydrogen should be produced by dissociation. Ionization or radiation at critical potentials of *atomic* hydrogen should be greater, relatively to effects due to molecular hydrogen, if this grid is hot.

*Method of Distinguishing between Effects of Radiation and Ionization.*—The receiving electrode could be either (1) a wire point of very small area, or, (2) a disk of large area. The former is relatively insensitive to effects of radiation since little radiant energy strikes it.

*Critical Potentials of Hydrogen.*—Thus, it is shown that 13.5 volts is the

ionizing potential of the *hydrogen atom*. There are two critical potentials near 11 volts; *ionization of the molecule* (probably without dissociation) at about 11.5 volts, and a weaker effect, ascribed to radiation from the atom, at about 10.2 volts. The strongest effect, dissociation of the molecule, and ionization of one of its parts, is put at 16 volts. Accurate experiments and special averaging methods were necessary, since the amount of atomic hydrogen produced by the incandescent grid was relatively small.

PRINCETON UNIVERSITY.

## 11. LOW-VOLTAGE ARCS IN DIATOMIC GASES AND THE EFFECT OF DISSOCIATION IN A TUNGSTEN FURNACE.

BY O. S. DUFFENDACK.

*Meaning of an Arc.*—When the space charge surrounding an incandescent cathode is neutralized by positive ions, the arc strikes and a redistribution of electric intensity, giving a large drop in potential near the cathode, results. This enables an electron to ionize a molecule at its first impact, and so an arc can be maintained at the ionizing potential, or lower if the molecules are already partially ionized.

*Average Breaking Potentials in Hydrogen and Nitrogen.*—In hydrogen and nitrogen the average potentials of the breaks of arcs between a filament and a plate were 16.35 and 16.16 volts, respectively, which are within the range of ionizing potentials of the molecules reported for these substances. As Bohr's theory puts the ionizing potential of the hydrogen atom at 13.52 volts and the radiating potential at 10.14 volts, it seemed that it should be possible to maintain the arc at these voltages if there were sufficient monatomic hydrogen present.

*Arcs in Monatomic Hydrogen.*—When a tungsten furnace was employed, giving from 27 per cent. to 90 per cent. dissociation at 2000° K. to 2500° K., the arc was maintained to 14 volts and the curves for the thermionic currents show sharp discontinuities at about 10, 14, and 16.5 volts.

PRINCETON UNIVERSITY.

## 12. MAGNETIC CONTROL OF THERMIONIC EMISSION FROM A STRAIGHT WIRE BY CURRENT IN THE WIRE.

BY ALBERT W. HULL.

Mathematical analysis of the motion of electrons from a straight wire to a concentric cylinder shows that the electrons will reach the cylinder if the ratio of potential difference to current in the wire is greater than a critical value, and will fail to reach it if the ratio is less than that value.

The critical value of current is

$$I = \frac{E_2^{\frac{1}{2}}}{\sqrt{2\frac{e}{m}} \log \frac{R}{r_0}},$$

where $E$ is the potential difference and $R$ and $r_0$ the radii of cylinder and wire.

This relation has been verified by experiments with tungsten-wire filaments up to 2.5 mm. diameter, using the heating current as control current. The results are shown by volt-ampere curves for constant-filament current, and oscillograms for alternating filament current.

For a tungsten filament of diameter $d$ cm. at 2500° K., heated by direct current, the critical voltage is

$$E = 5310 d^3 \left( \log_{10} \frac{R}{r_0} \right)^2 \text{ volts.}$$

This is negligible for a 1/4 mm. (10 mil) filament, but is approximately 10,000 volts for a 5 mm. filament in a 10 cm. cylinder, and nearly 100,000 volts for a 1 cm. filament.

RESEARCH LABORATORY,
GENERAL ELECTRIC CO.,
SCHENECTADY, N. Y.,
February 8, 1922.

## 13. A TEST OF THEORIES OF CUMULATIVE IONIZATION.

BY K. T. COMPTON.

*Current Preceding Striking of Arc.*—Using the equation

$$n/n_0 = 1/(1 - 4\sqrt{3680 M P_0})$$

for the current $n$, in terms of the current $n_0$ if there were no ionization, the molecular weight $M$ of the gas and the probability $P_0$ of partial ionization of a molecule, values of $P_0$ were calculated for ionization in helium at various pressures, currents and voltages.

*Ionization by Successive Impacts.*—These values of $P$ are substituted in the equation derived by the writer for ionization by successive impacts to test its adequacy. The conclusion is definitely reached that successive impacts play an unimportant rôle in cumulative ionization.

*Photo-impact Ionization.*—A similar test of this theory shows that it is consistent with the experiments, and indicates that $\tau/\rho^2$ is about 0.08 for helium. $\tau$ is the time interval between excitation of an atom and its emission of resonance radiation, and $\rho$ is the reciprocal of the absorption coefficient for this radiation in the gas at 1 mm. pressure.

PRINCETON UNIVERSITY.

## 14. THE SCATTERING OF ELECTRONS BY ALUMINUM.

BY C. DAVISSON AND C. H. KUNSMAN.

A PRELIMINARY note on "The Scattering of Electrons by Nickel" was published by the writers in Science for Nov. 25, 1921. Similar observations have now been made on the scattering of electrons by aluminum. For bom-

barding potentials up to 200 volts the maximum intensity of scattering is back along the path of the primary beam; there is no lateral maximum as in the case of nickel, and the distribution is well represented by the relation

$$I_\Psi = k\left[\frac{2\beta - 1}{(2\beta - 1)^2(1 + \cos\Psi) + (1 - \cos\Psi)}\right]^2.$$

These results were expected since the aluminum atom is characterized by only a single strong shell of electrons. Above 200 volts the distribution appears to be the sum of two simple distributions. The added distribution is thought to comprise electrons scattered by atoms of oxygen on the surface of the target. In the compound $Al_2O_3$ each oxygen atom has a net charge $-2e$ which may be expected to prevent electrons of speeds less than 150 or 200 volts from entering them. It follows that no strong back scattering due to oxygen should occur until this voltage has been passed.

Analysis of the distribution curves below 200 volts indicates that the L-electrons in the aluminum atom are at a distance of about $3 \times 10^{-9}$ cm. from the nucleus.

RESEARCH LABORATORIES OF THE
AMERICAN TELEPHONE AND TELEGRAPH COMPANY,
AND THE WESTERN ELECTRIC COMPANY, INC.,
January 30, 1922.

## 15. THE RATIO OF THE TWO ELEMENTARY CHARGES.

BY F. W. LOOMIS.

SINCE the oil drops in Millikan's experiments were exactly neutral $\pm$ a small integral number of elementary charges, to 1/1000 of an electron, and since they contained as many as $4 \times 10^{14}$ protons and nearly the same number of electrons, it follows that the magnitudes of the charges on protons and electrons are equal to one part in $4 \times 10^{17}$.

NEW YORK UNIVERSITY.

## 16. IONIZATION AND RADIATION POTENTIALS AND THE SIZE OF THE ATOM.

BY BERGEN DAVIS.

A NOTE recently published by Prof. A. S. Eve (Nature, June 30, 1921), points out a possible relation between the ionization potential and the size of the atom.

For some time I had been accumulating data for a similar comparison but from a somewhat different point of view. Eve considers that the outer electron ring is the boundary of the atom. I here assume that the limit of the atom extends beyond this to the point to which an electron must be lifted to produce radiation. If $a$ is the radius of this electron ring and $b$ is the distance from the atomic center that an electron must be lifted to produce radiation, then

$$R = \frac{A}{a} - \frac{A}{b}$$

and

$$I - R = \frac{A}{b}$$

where $A$ is a constant.

The product $(I - R) \times b$ or, for comparison with atomic volumes, $(I - R)\sqrt[3]{\text{A.V.}}$ should be a constant. This product is found to be nearly a constant for elements of the first group. Quite constant for those of the second group. Fairly constant for the inert gas group. The other groups do not show so good constancy. On the whole the product $(I - R)\sqrt[3]{\text{A.V.}}$ is more nearly constant than the product $I\sqrt[3]{\text{at.V.}}$ as proposed by Eve. Paper will be published in detail later.

PHŒNIX PHYSICAL LABORATORY,
COLUMBIA UNIVERSITY.

## 17. ON THE SPECTRA OF X-RAYS OF SHORT WAVE-LENGTHS.

BY WILLIAM DUANE AND K. C. MAZUMDER.

THIS paper contains an account of experiments on the spectra of x-rays of short wave-lengths, which are now being used extensively in the treatment of malignant and other diseases that lie some distance below the skin.

The x-ray plant, including the spectrometer, has been described in previous papers.

Curves were shown illustrating the distributions of energy in spectra of x-rays produced by constant and alternating voltages of about 165,000 volts. Other conditions being the same, the constant voltage gives a much more intense beam of x-rays than the alternating voltage does. It produces, also, a better distribution of energy in the spectrum, *i.e.*, a greater proportion in the short wave-lengths.

Experiments with various absorbing substances (filters) interposed between the x-ray tube and the spectrometer indicate that copper filters give a much better spectrum than aluminium, and somewhat better than filters composed of compounds of a chemical element of mean atomic weight (such as lanthanum) with one of low atomic weight (such as chlorine) do.

The following table contains the mass coefficients of absorption, $\mu/\rho$, for x-rays of different, short wave-lengths.

| Wave-Length, $\lambda$. | Mass Coefficient of Absorption, $\mu/\rho$. | |
|---|---|---|
| | Copper. | Aluminium. |
| .1653 | 1.015 | .218 |
| .1477 | .745 | .194 |
| .1381 | .631 | .189 |
| .1290 | .538 | .182 |
| .1124 | .399 | .167 |
| .0951 | .299 | .161 |

The values of the coefficients given by Richtmyer[1] for the wave-length .135 agree with the data in the above table to within a few per cent.

In a paper presented to the Physical Society in 1914 it was shown by one of us that over a wide range of wave-lengths (extending down to .4) the coefficients of absorption for aluminium could be quite well represented by the equation $\mu/\rho = 14.9\lambda^3$. According to Hull and Rice[2] an equation of the form

$$\mu/\rho = k\lambda^3 + s \qquad (1)$$

approximately represents the coefficients between the wave-lengths .392 and .147. If we plat our values of the coefficients against the cubes of the wave-lengths the curves representing them are not quite straight lines. They bend downward slightly in the region of short wave-lengths. Our data, however, may be approximately represented by equation (1), if we put $k = 193$ and $s = .13$ for copper, and $k = 15.5$ and $s = .147$ for aluminium. According to the usual interpretation (which may turn out to be somewhat artificial) $s$ represents the mass scattering coefficient.

The thickness of aluminium that absorbs the same fraction of x-radiation as a given thickness of copper depends upon the wave-length. For the wave-length .44 the ratio of the two thicknesses is about 31, whereas for wave-length .095 it is only 6. This fact has enabled us to devise a simple method of estimating quickly the average, or "effective" wave-length of a beam of rays that is not homogeneous. The method consists in measuring by means of an ionization chamber, a photographic plate or a phosphorescent screen the relative thicknesses of aluminium and copper that absorb the same amount of the energy in the beam. A curve gives the corresponding wave-length. The relation between the ratio of the two thicknesses and the wave-length may be obtained from equation (1) by taking the ratio of the two linear coefficients of absorption and putting in the proper values of the constants, $k$ and $s$. The densities of the copper and aluminium used were 8.92 and 2.7 respectively.

HARVARD UNIVERSITY.

## 18. THE CRYSTAL STRUCTURE OF SILVER-PALLADIUM AND SILVER-GOLD ALLOYS.

BY L. W. MCKEEHAN.

IT is well known that palladium alloys with silver in all proportions forming a continuous series of solid solutions, that crystals of each of these metals possess face-centered cubic space lattices, and that the edge of the unit cube in palladium is about four per cent. less than that in silver. It is also well known that gold alloys with silver in all proportions forming a continuous series of solid solutions, that crystals of gold possess a face-centered cubic space lattice, and that the edge of the unit cube in gold is not more than one per cent. greater than that in silver.

[1] PHYSICAL REVIEW, (2), XVIII, p. 13.
[2] PHYSICAL REVIEW, (2), VIII, p. 326.

An x-ray analysis of two graded series of alloys extending from pure silver to pure palladium, and from pure silver to pure gold shows that the edge of the unit cube in silver decreases progressively with the addition of palladium, but remains practically unchanged by the addition of gold. The effects of cold-work and of annealing have been observed. Accurate values for the edges of the unit cubes, and the corresponding densities of the pure metals and alloys have been obtained.

RESEARCH LABORATORIES OF THE
AMERICAN TELEPHONE AND TELEGRAPH CO.,
AND THE WESTERN ELECTRIC COMPANY, INC.,
January 31, 1922.

## 19. PRECISION MEASUREMENT OF CRYSTALS.

BY WHEELER P. DAVEY.

BY simultaneously recording the x-ray diffraction pattern of NaCl on one half of a film, and the pattern of some other crystal on the other half of the same film, it is possible to determine the dimensions of the second crystal in terms of the dimensions assumed for NaCl. On any one film the results so obtained are consistent among themselves. This may be shown by plotting the results on "probability paper." Values of crystal dimensions obtained from different films at different times agree to within one tenth of one per cent.

By this method the side of the body centered cube of CsBr is found to be 4.287 Å. The side of the simple cube (NaCl structure) of RbI is 3.654 Å.

RESEARCH LABORATORY,
GENERAL ELECTRIC COMPANY,
SCHENECTADY, NEW YORK.

## 20. A SPECTROGRAPHIC STUDY OF ULTRAVIOLET FLUORESCENCE EXCITED BY X-RAYS.

BY J. O. PERRINE.

IN the phenomenon of fluorescence, the emitted radiation has a greater wave-length than the exciting radiation. Therefore, with x-rays as the incident radiation it is not unlikely that fluorescence in the ultraviolet region would result. With this idea as a working basis, a large number of substances were subjected to x-rays and with the aid of an ultraviolet spectrograph, the photographic plate recorded whatever ultraviolet fluorescence there might be.

Fourteen samples of the double salts of uranium, twenty-three oxides and fifty-four samples of miscellaneous salts gave negative results. Exposures varying from one half hour to fifteen hours were made with a Coolidge tube operating at 2 milliamperes, 50,000 volts.

The chlorides of potassium, lithium, rubidium, sodium and caesium gave positive results. Sodium chloride has a very strong band at a wave-length 2,470 Å. Caesium chloride gave the best results with a strong band extending from 5,720 to 2,340 Å. with three points of maximum intensity.

Several samples of willemite were examined, some of which gave positive results. Calcium tungstate, three x-ray intensifying screens and one fluoroscopic screen were examined with varying results.

Quantitative measurements were made of the blackening on the photographic plate by means of a photo-electric cell photometer. Curves showing the distribution of blackening throughout the fluorescent band were plotted, thereby locating the points of maximum intensity.

AMERICAN TELEPHONE AND TELEGRAPH COMPANY.

## 21. THE GRATING SPACE OF MICA AND THE INTENSITIES OF THE SPECTRAL ORDERS.

BY BERGEN DAVIS AND H. M. TERRILL.

THE grating space of this specimen of mica was measured by an ionization spectrometer in the usual manner. Determinations were made over a number of orders, in one instance to the seventh order.

At the same time measurements were made of the relative intensities of the $\alpha_1$ and $\beta_1$ lines in the various orders. $K$ characteristic of molybdenum.

The grating space was found to be 9.845 Å. for determinations at the first order, increasing to 9.958 at the seventh order. This increase was progressive. This change of grating space with order has been observed by Stenström, who attributes the effect to a small refraction of the x-rays in the crystal. This is not, however, the only explanation. It may readily be shown that a very small curvature of the crystal will produce this effect. The direction of the progressive change in the grating space with order will depend in this case on whether the crystal is slightly convex or concave.

The intensities of the spectral orders showed that the odd spectra were more intense than the even orders, as observed by de Broglie.

The intensities of the $\alpha_1$ line in the several orders was as follows: (1) 364, (2) 221, (3) 544, (4) 175, (5) 508, (6) 28, (7) 101.

The average intensity of the $\alpha_1$ line was about 3.5 times that of the $\beta_1$ line.

This paper will be published in detail later.

PHŒNIX PHYSICAL LABORATORY,
COLUMBIA UNIVERSITY.

## 22. A NEW TYPE OF BUMSTEAD ELECTROMETER AND ACCESSORY APPARATUS.

BY HARRY CLARK.

THE gold-leaf of this electrometer is not adjustable. The charged plates are 60° sectors of cylindrical tubes, and they are so placed that the concave surfaces face the leaf and the lower edges are close together underneath the leaf. Each of the plates may be moved vertically by means of a micrometer screw. The instrument can therefore be adjusted quickly to any degree of sensitivity while the leaf is kept on any desired part of the scale. When the highest sensitivity is not required, the settings may be duplicated by means

of the screw readings. The shape and position of the plates and the limits of their adjustment are such that accidental contact of the leaf with the plates is impossible. The electrometer has been combined with standard condensers, earth and voltage connections, and a device for attaching various ionization chambers. It has been mounted adjustably on a movable base so that it can be put easily to a great variety of uses.

THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH,
NEW YORK CITY.

## 23. DYNAMIC CHARACTERISTICS OF HELIUM ARCS.

BY FABIAN M. KANNENSTINE.

HELIUM arcs were formed by impressing a 60-cycle alternating e.m.f. between a Wehnelt cathode and nickel plate in a pyrex tube containing pure helium.

The relation between the e.m.f. impressed and the current through the arc was obtained by Braun tube oscillograms. The arc struck at about 21 volts and the current through the arc increased as the impressed e.m.f. increased in much the same manner as found by K. T. Compton, E. G. Lilly and P. S. Olmstead.[1] However as the voltage decreased quite different results were obtained from those obtained by the above-mentioned authors.

The decreasing part of the curve was above the increasing part and formed a loop, while the arc, instead of breaking at 20 volts, broke at or near zero volts. The decreasing curve instead of being smooth had two sudden changes in curvature, one at or near zero and the other considerably higher but below the striking potential.

These curves seem to indicate that in the arc products are formed which have a very low ionization potential, and a short but measurable life period.

UNIVERSITY OF CHICAGO.

## 24. THE JOULE EFFECT IN STEEL RODS AT DIFFERENT DRAWING TEMPERATURES.

BY S. R. WILLIAMS AND O. KOPPIUS.

IN this paper a study has been made of the Joule effect in a group of five steel rods at different drawing temperatures. These rods had the following chemical analysis:

| Rod No. | Carbon. | Manganese | P. | S. | Si. |
|---|---|---|---|---|---|
| 1..... | 1.34 | 0.37 | 0.010 | 0.018 | 0.13 |
| 3..... | 1.27 | .27 | .... | .... | .... |
| 4..... | 1.23 | .32 | .... | .... | .... |
| 5..... | 1.35 | .34 | .... | .... | .... |
| 6..... | 1.27 | .37 | .... | .... | .... |

[1] PHYSICAL REVIEW, (2), XVI, p. 282.

It was interesting to find that beginning with one rod quenched in oil at 788° C. and not annealed there was no initial lengthening as is common to steel, but only as the rods were subjected to higher and higher annealing temperatures did this initial elongation occur. This is important not only for the metallographer but has a great deal of significance for the theory of the process of magnetization in steel rods.

OBERLIN COLLEGE.

## 25. EFFECTS OBTAINED WITH AN ALTERNATING CURRENT SENT THROUGH A CAPILLARY ELECTROMETER.

BY R. D. KLEEMAN AND D. T. SIMMONDS.

A CAPILLARY electrometer was used consisting of a more or less horizontal capillary tube in which mercury and a saturated solution of mercurous sulphate containing one volume of sulphuric acid to seven of water were in contact, the thread of mercury ending in a reservoir of mercury making contact with one of the electrodes, and the thread of solution ending in a reservoir of solution having mercury at the bottom which made contact with the other electrode. An alternating current sent through the electrometer gave rise to a motion of the mercury-solution interface in the same direction as that obtained with a direct current from solution to mercury. Both increase the interfacial surface tension, and thus decrease the electrical double layer, the positive side of which faces the mercury. The alternating current is partly rectified, but the direct current component is in a direction that would tend to make the interface move in the opposite direction. It arises from the fact that the alternating current density across one of the mercury surfaces is much less than that across the other, which gives rise to the corresponding electrical layers being decreased to different extents, giving rise to a difference of potential between them. This shows that a part at least, if not the whole, of the e.m.f. between a metal and a solution is located in the liquid transition layer, as proposed by a theory published in a previous paper.

On putting a condenser in the circuit to cut out the direct current and measuring the pressure necessary to apply to the mercury to keep the interface in position, it was found that the pressure increased approximately linearly up to 10 cms. of mercury which corresponded to about 1.2 volts, above which no change in pressure with change of voltage was obtained. A maximum pressure of 23 cms. of mercury was obtained with a direct current, which also corresponded to 1.2 volts.

UNION COLLEGE,
SCHENECTADY, N. Y.

## 26. NOTE ON THE FORMATION OF NEGATIVE IONS IN A GAS.

BY R. D. KLEEMAN.

MEASUREMENTS of the velocity of negative ions in a gas subjected to an electric field usually give larger values at low pressures than inversely propor-

tional to the pressure. This effect, which has been investigated by a number of physicists, is intimately connected with the nature of the formation of ions from free electrons. Loeb has carried out a careful set of experiments (PHYSICAL REVIEW, Vol. XVII., 1921, pp. 89–115) to distinguish between the theory that each liberated electron forms a permanent ion after a certain period (Thomson's theory), and the theory that some of the electrons never get into a suitable state to form ions, while the rest form permanent ions (Wellisch's theory). The experimental results were interpreted to support the former theory. The object of this paper is to point out that Loeb's results, and in general the effect under various conditions, can be as well explained by the theory of ion formation and existence proposed by the writer (Proc. Camb. Phil. Soc., Vol. XVI., pt. 4, pp. 285–298 (1911), and Vol. XVII., pt. 3, pp. 263–279 (1913). According to this theory the electron continually goes through cycles of ion formation and dissociation, during which it is periodically in the free state. This theory, besides, explains a number of other effects.

UNION COLLEGE.

## 27. NOTE ON X-RAY SPECTRA.

BY WILLIAM DUANE AND R. A. PATTERSON.

*L Absorption Limits.*—The following table contains new and more accurate measurements of the $L_2$ and $L_3$ absorption limits for Au, Pt, and Bi.

TABLE I.

*Critical Absorption. L Series of X-Rays.*

Grating Space for Calcite, $2d = (6.056 \pm .004) \times 10^{-8}$ cm.

| Chemical Element. | $L_2$. | | $L_3$. | |
|---|---|---|---|---|
| | $\lambda \times 10^8$ cm. | $\nu/\nu_\infty$. | $\lambda \times 10^8$ cm. | $\nu/\nu_\infty$. |
| Pt..... | .9318 ± 3 | 0.9779 | .8918 ± 9 | 1.022 |
| Au..... | .9008 ± 4 | 1.0116 | .8610 ± 9 | 1.058 |
| Bi..... | .7871 ± 4 | 1.1578 | .7562 ± 9 | 1.205 |

The bearing of these new data on the relations between absorption and emission frequencies is discussed. It is shown that these new values lend support to the x-ray spectra systems proposed by Smekal and Coster.

The relation that an $L$ absorption frequency minus an $M$ absorption frequency should equal an $L$ emission frequency has been shown by us to be approximately true for those cases not eliminated by a "selection principle." With his new and accurate measurements Coster has shown that there is a systematic deviation from the above relation. He ascribes this deviation to the fact that our values for the $L$ absorption frequencies are too small because we have measured the centers of the "drops" in ionization currents due to absorption limits. He and other investigators have found "white lines"

near the absorption limits on their photographic plates and he suggests that the center of this white line constitutes the true position of the absorption limit. We have not yet found any indication of this white line on our ionization current graphs.

*The K Series Spectrum of Molybdenum.*—Table II. contains our values for the emission and absorption wave-lengths in the $K$ series of Mo. Overn's recent measurements of the emission lines are also given.

TABLE II.

*K Series of Molybdenum.*

Grating Space for Calcite, $2d = 6.056 \times 10^{-8}$ cm.

| Line. | Overn. | Duane-Patterson. | Δ. | Ratio of Intensities. |
|---|---|---|---|---|
| $\alpha_2$..... | .7129 | .71213 ± 8 | .0008 | |
| $\alpha_1$..... | .7085 | .70783 ± 7 | .0007 | $\frac{\alpha_1}{\alpha_2} = 1.93$ 2d order |
| $\beta'$..... | .... | .6320 ± 2 | .... | $\frac{\beta}{\gamma} = 6.3$ 1st order |
| $\beta$..... | .6322 | .63114 ± 7 | .0011 | |
| $\gamma$..... | .6212 | .6198 ± 2 | .0014 | $\frac{\beta}{\gamma} = 5.5$ 2d order |
| $K$..... | .... | .6184 ∓ 2 | .... | |

They have been corrected slightly to correspond to the calcite grating space. In the fourth column are given the differences between Overn's values and ours. Overn measured all his lines relative to a reference line at $\lambda = 0.7956$ which value is independent of any x-ray measurements. The values of $\Delta$ indicate that our measurements deviate more from Overn's the farther we go away from his reference line.

In the last column of Table II. are the relative intensities of $\alpha_1$ and $\alpha_2$, and also of $\beta$ and $\gamma$. The value 1.93 for the ratio of $\alpha_1$ to $\alpha_2$ is in close accord with Bohr's predicted ratio of 2.0.

HARVARD UNIVERSITY.

## 28. ELECTRIC FIELDS DUE TO THE MOTION OF CONSTANT ELECTROMAGNETIC SYSTEMS.

BY S. J. BARNETT.

A SYSTEM $B$ has velocity $v$ relative to fixed axes $C$. $E$, $E'$, $H$, $H'$, $\psi$, $\psi'$, $A$, $A'$ are the electromotive and magnetic intensities, and the electric and vector potentials, observed in $C$ and $B$, at a point fixed in $C$. $E = -\partial A/\partial t - \nabla\psi$, $E' = -\partial A'/\partial t - \nabla\psi' - [vH']$. Assuming a principle of relativity $E = E'$, $H = H'$, Maxwell proved that the motion produces in $C$ an electric potential $\psi - \psi' = (Av)$. For a constant system, unelectrified in $B$, $\partial A'/\partial t = 0 = \nabla\psi'$, and $\partial A/\partial t = -(v\nabla)A$; so that $E = (v\nabla)A - \nabla(Av) = E' = [Hv]$. This paper derives from $A$ and $v$ the electric fields for a number of cases. Examples follow. I. Two parallel wires with currents $\pm I$, $v$ being parallel to $I$.

Here $\partial A/\partial t = 0$ and $E = -\nabla(Av)$. The motion produces charges $\pm q = \pm Iv$ per unit length along the wires. II. Two plane parallel sheets with currents $\pm I$ per unit length, $v$ being parallel to the streamlines. Between the sheets the electric field is uniform and normal to $v$, the charges per unit area being $\pm q = \pm Iv$. Again $E = -\nabla(Av)$. In both I. and II. the electric moment produced is the vector product of $v$ and the magnetic moment. III. An infinite uniform circular cylindrical current sheet, with magnetic moment $M$ per unit length, and $v$ normal to the axis. $(Av)$ is such as to produce a uniform field with intensity $1/2[Hv]$ within the cylinder, and without the cylinder the field of an axial electric line doublet with moment $[vM]$. $(v\nabla)A$ doubles the intensity inside and cancels it outside. IV. A spherical current sheet with magnetic moment $M$ and current $I$ per unit length of the diameter, $v$ being normal to the magnetic axis. Inside $(Av)$ gives a uniform intensity $-\nabla(Av) = 1/2[Hv]$; outside, the field of a central electric point doublet with moment $[vM]$. $(v\nabla)A$ alters the intensity to $[Hv]$ everywhere. V. Two cylindrical coaxial magnetic poles with a radial field between them, $v$ being parallel to the axis. Here $(Av) = 0$, there are no charges, and $E = (v\nabla)A = [Hv]$. If any system is charged in $B$, $\psi'$ must be added to $(Av)$. Conductors added to $B$, and uncharged in $B$, do not alter $\psi - \psi'$.

THE CARNEGIE INSTITUTION OF WASHINGTON.

## MINUTES OF THE MEETING AT STANFORD UNIVERSITY, MARCH 4, 192.2

THE 114th regular meeting of the American Physical Society was held in the lecture room of the Department of Physics, Stanford University, at 1:30, March 4, 1922. Professor Fernando Sanford presided. About 30 members and friends were in attendance. Dinner was served in Stanford Union at 6 o'clock.

The following program was presented:

1. A Note on the Estimation of Tenths. PAUL KIRKPATRICK.

2. The Penetration of Cathode Rays in Molybdenum and its Effect on X-Ray Spectra. D. L. WEBSTER.

3. A Device for Timing Ionization Currents Accurately. D. L. WEBSTER.

4. The Absorption Spectrum of Chloroform in the Near Infra-Red. J. W. ELLIS.

5. On the History of Caloric. FLORIAN CAJORI.

6. A Lunar Diurnal Variation of Earth Potential and Earth Currents. FERNANDO SANFORD.

7. On the Displacement of the North Magnetic Pole of the Earth from the North Geographic Pole. FERNANDO SANFORD.

8. New Spectra of Oxygen and Nitrogen in the Extreme Ultraviolet. J. J. HOPFIELD.

9. A Modification of van der Waal's Equation. W. P. BOYNTON and ARTHUR BRAMLEY. (Read by title).

10. Relativity and the Ether. S. R. COOK.

11. Examples of Motions which have a Terminal Speed. W. J. RAYMOND. Read by title).

12. Restriction of the Electron Beam from a Hot Cathode Braun Tube. L. T. JONES and H. G. TASKER.

13. A Constant Resistance Universal Shunt. H. G. TASKER.

14. The Standardization of Permanent Magnets. RICHARD HAMER.

15. The Effect of Temperature Changes on Rubber Colloids. RICHARD HAMER.

E. P. LEWIS,
*Local Secretary for the Pacific Coast.*

## 1. A NOTE ON THE ESTIMATION OF TENTHS.

BY PAUL KIRKPATRICK.

IT was supposed that systematic errors of a particular kind might occur in the process of estimating tenths of the interval between two parallel lines. This supposition was tested by several hundred attempted settings within such an interval one centimeter in width on an instrument made for the purpose.

The results with fifty-nine observers, each making nine different settings, was as follows:

The absolute accuracy of settings, irrespective of the signs of the errors, was highest at the five-millimeter position and lowest at seven millimeters and three millimeters.

The settings of the average observer are given herewith:

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Attempted settings..... | .100 | .200 | .300 | .400 | .500 | .600 | .700 | .800 | .900 |
| Actual settings..... | .110 | .203 | .322 | .420 | .502 | .583 | .677 | .795 | .893 |

It is seen that the average observer tended always to draw away from the nearer scale ruling. It may be shown in consequence that with observers of this class on the scale here used the probability that a random setting should be ascribed to the wrong millimeter is about .12.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF CALIFORNIA.

## 2. THE PENETRATION OF CATHODE RAYS IN MOLYBDENUM, AND ITS EFFECT ON THE X-RAY SPECTRUM.

BY DAVID L. WEBSTER.

THE penetration of cathode rays in molybdenum was investigated by studying the emission spectrum around the $K$ absorption limit. The stronger absorption on the short-wave side of this limit reduces the emission intensity by about 8 per cent. at 25 kv. and about 16 per cent. at 70 kv., when the cathode rays go in at about 45° to the surface and the x-rays emerge at the same angle. As no rays of this wave-length are produced by electrons of less than 20 kv. energy, the 8 per cent. at 25 kv. may be due largely to surface irregularities, which must be of the order of a micron. The increase at higher voltages measures the average depth of penetration of the cathode rays, which runs up to about 2 microns or so at 70 kv. This is less than one tenth of the depth

one would predict from Whiddington's work on aluminum and gold; but that work was concerned only with the fastest components of a beam after emerging from a metal leaf, so at least a part of this difference must be due to the difference between the average depth and that of the rays that go straightest.

STANFORD UNIVERSITY, CALIF.,
March 4, 1922.

## 3. A DEVICE FOR TIMING IONIZATION CURRENTS ACCURATELY.

BY DAVID L. WEBSTER.

THE purpose of this paper is to call attention to the possibility of eliminating the human element in the timing of ionization currents in an x-ray spectrometer, by a simple device made from 3 electric bells and a clock escapement. One bell magnet drives the clock escapement with current from a good pendulum clock. The ratchet wheel driven by this escapement carries 2 pins, each of which makes contact with a brush, for one current impulse only. This contact is made at the release of the escapement magnet, and is therefore ready when the next clock current impulse arrives. This next clock current impulse goes from the pin to a magnet that works a lead shutter in the path of the x-ray beam. Thus the accurate timing is done by the master clock, the electric clock merely serving to select the current impulse that will be used.

STANFORD UNIVERSITY, CALIF.,
March 4, 1922.

## 4. THE ABSORPTION SPECTRUM OF CHLOROFORM IN THE NEAR INFRA-RED.

BY J. W. ELLIS.

To study the region 1.0 $\mu$ to 2.8 $\mu$ a spectrograph of the auto-collimation type was constructed with two 30° medium flint glass prisms through which the radiation from a 108-watt tungsten lamp passed twice. A bismuth-silver thermopile and a Leeds-Northrup movable-coil galvanometer were used.

Readings were taken as the radiation passed alternately through an empty glass cell in front of a 0.5 millimeter slit and a similar cell filled with chloroform of three millimeters thickness. Correction was made for internal reflection.

In this region lines at 1.011 $\mu$, 1.066 $\mu$, and 1.165 $\mu$ were found by Abney and Festing, and absorption maxima at 1.916 $\mu$ and 2.652 $\mu$ by Iklé.

In the present work five distinct bands were observed with maxima at 1.140 $\mu$ (10 per cent.); 1.385 $\mu$ (16 per cent.); 1.660 $\mu$ (56 per cent.); 1.835 $\mu$ (35 per cent.); 2.425 $\mu$ (88 per cent.). Per cent. absorption is given in brackets.

These values should be correct to within 100 Å. The calibration curve was drawn through points representing 10 metallic emission lines and 9 infra-red solar absorption bands, determined mainly by Paschen with a grating. The average deviation of these points from the smooth curve is less than 50 Å.

The chloroform was manufactured by Squibb's Manufacturing Company and was rated as exceptionally pure.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF CALIFORNIA.

## 5. On the History of Caloric.

By Florian Cajori.

1. Lucretius must be placed in the list of those who taught the existence of a ponderable heat-substance.

2. Caloric is not an eighteenth-century offspring of phlogiston (as has been claimed); the word "caloric" was coined about 1789, but caloric substances (assumed by some to be ponderable, by others imponderable) are older than phlogiston; no clear views existed on the interrelation of phlogiston and caloric.

3. In America, Hugh Williamson of Philadelphia in 1770 explained heat as due to "rapid vibrations of minute particles"; Benjamin Franklin in 1788 suggested that the subtle fluid, whose vibration is called light, strikes common matter and causes heat; Robert Hare of Philadelphia in 1822 and Denison Olmsted of Yale in 1826 held the materialistic theory of heat; in B. Silliman's books, heat is an "imponderable agent" in 1830, but due to "vibratory movements of molecules" in 1859.

University of California.

## 6. A Lunar Diurnal Variation in Earth Potential and in Earth Currents.

By Fernando Sanford.

A previous report of observations on a lunar variation of earth potential at Palo Alto was published in Physical Review of October, 1921. The observations there described have been continued. The mean daily range of variation in electrostatic potential of the earth for ninety lunar days in the months of September, October, November and December, 1921, has been, after the solar variation was eliminated, five millimeters on the photographic record, which is equivalent to introducing 1/10 volt between the earth and the electrometer. The effect of the varying distance of the moon from the earth is plainly appreciable. For the four months cited the lunar variation at perigee is 1.4 times as great as at apogee.

By arranging the data on the diurnal variation of the N-S earth-current at Tortosa, Spain, according to lunar days, the influence of the moon on this current is shown. The mean lunar variation in potential difference between the grounded extremities of the line was 18.5 millivolts/kilometer for 27 days in October, 1920. The data used are from Vol. XI., of the Bulletin of *Observatorio del Ebro.*

## 7. On the Displacement of the North Magnetic Pole of the Earth from the North Geographic Pole.

By Fernando Sanford.

If the primary magnetic field of the earth is due to the rotation of its negative charge, its magnetic axis should approximately coincide with its geographical

axis. It is characteristic of the earth-currents which have been observed that the electrons move around the earth in the direction of the sun's apparent motion. The effect of this induced current around the earth is to weaken the primary magnetic field.

Since the water of the sea is a better conductor of electricity than are the solid materials of the earth, these induced currents will take a water route in preference to a land route. The most nearly continuous east and west water route around the earth will pass about 15 degrees north of the Equator on the American side and about an equal distance south of the Equator on the Asiatic side. Currents flowing from west to east around this route will induce a magnetic field opposite in character to the primary field and with its northerly pole on the Asiatic side of the geographical pole. The resultant northerly pole will accordingly be displaced toward the American side of the geographical pole.

## 8. NEW SPECTRA OF OXYGEN AND NITROGEN IN THE EXTREME ULTRAVIOLET.

BY J. J. HOPFIELD.

THE spectrum of oxygen was extended from the former value, λ 990, to the new value, λ 508. Some of the short wave-lengths obtained are approximately (accurate values will be published later) 508, 539, 554, 582, 601, 610, 611, 618, 626, 646, 675, 688, 705, 706, 721, 766, 767, 778, 792, 799, 835, 837. and then 150 lines between 837, and 1,335 Å. This spectrum was obtained with a disruptive discharge at low pressure, the oxygen being pumped through the receiver and connected discharge tube during the exposure. Some of the lines listed above check those obtained by Millikan.

By using a discharge tube of the internal capillary type, but of 2.25 K.W. capacity, with electrodes and capillary oil cooled, the spectrum of nitrogen was extended from 1,400 to 825, and lines at 307 and 362 were also photographed.

The spectrum of air was obtained with the same tube at a pressure of 3 mm. with two minutes exposure to 1,050 Å. These facts,—that by using a powerful discharge the time of exposure can be shortened from one or two hours to as many minutes, and that air does not have prohibitive absorption,—suggest the practicability of building a vacuum grating spectrograph containing a long focus grating. Such a spectrograph, despite its limitations, would be of great usefulness.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF CALIFORNIA.

## 9. A MODIFICATION OF VAN DER WAALS' EQUATION.

BY W. P. BOYNTON AND ARTHUR BRAMLEY.

THE equation for an ideal gas and van der Waals' equation are excellent first and second approximations. A third approximation is suggested:

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT\,\frac{T^2/\psi^2}{1 + T^2/\psi^2},$$

which fits Andrews' data on carbon dioxide at least as well as does the equation of Clausius. The correction factor gives a graph resembling the rational curve for specific heats of solids given by Compton.[1]

[1] PHYSICAL REVIEW (2), VI, p. 377.

A study of the thermodynamic necessities for a specific heat *not* assumed to have a constant value leads to formulae for specific heat at constant volume, internal energy and entropy respectively:

$$C_v = 2R\,\frac{3T^2/\psi^2 - T^2/\psi^2}{(1 + T^2/\psi^2)^3}\,ln\left(\frac{v}{b} - 1\right) + f(T),$$

$$U = 2RT\,\frac{T^2/^2}{(1 + T^2/\psi^2)^2}\,ln\left(\frac{v}{b} - 1\right) - \frac{a}{v} + \frac{a}{b} + \int_0^T f(T)dT,$$

$$S = R\,\frac{3T^2/\psi^2 + T^2/\psi^2}{(1 + T^2/\psi^2)^2}\,ln\left(\frac{v}{b} - 1\right) + \int_0^T \frac{f(T)}{T}\,dT.$$

We have for the final terms of our solutions

$$f(T) = M\,\frac{k^2T^2}{1 + k^2T^2},$$

$$\int_0^T f(T)dT = M\left(T - \frac{1}{k}\tan^{-1} kT\right),$$

$$\int_0^T \frac{f(T)}{T}\,dT = \frac{M}{2}\,ln(1 + k^2T^2).$$

This assemblage of equations closely approximates van der Waals' equation and the formulæ derived from it on the assumption of constant specific heat through the region of large volumes and high temperatures, gives the same relations for critical volume and pressure, and a somewhat more complicated one for critical temperature, but at low temperatures the specific heat and entropy approach zero values, as the latest studies show they should, so that the value of the entropy here given has no infinite constant of integration, but is finite for all finite values of temperature and volume.

UNIVERSITY OF OREGON,
EUGENE, OREGON,
February 20, 1922.

## 10. RELATIVITY AND THE ETHER.

BY S. R. COOK.

VARIOUS hypotheses of relativity are briefly discussed; and it is pointed out that if the ether drift experiment of Michelson, Morley and Miller, should be repeated it would be necessary to take into consideration not only the motions of the observer due to the motion of the earth in its orbit, and the motion of the sun in space, but also the probable motion of our galaxy in space.

Various theories of the ether are also discussed, and it is maintained that our

knowledge of the nature of the ether is such, that at present, any definite theory of relativity based upon the known properties of the ether or the velocity of light is premature.

COLLEGE OF THE PACIFIC.

## 11. EXAMPLES OF MOTIONS WHICH HAVE A TERMINAL SPEED.

BY WILLIAM J. RAYMOND.

THREE rectilinear motions are selected, involving constant driving force and either an increasing resistance or an increasing amount of effective inertia, real or fictitious. Speeds are (1) $v = c(1 - e^{-kt})$; (2) $v = c \tanh (kt)$; (3) $v = ct(k^2 + t^2)^{-1/2}$. The terminal speed is $c$. A model has been designed, a massive wheel driven by a descending weight, the speed of the latter retarded: (*a*) by an electromagnetic brake, giving resistance proportional to the speed; (*b*) by a mechanical brake, giving resistance proportional to the square of the speed; (*c*) by increasing moment of inertia of the wheel, caused by radially moving weights; (*d*) by wrapping the driving cord around a screw-threaded shaft, the radius of the shaft decreasing as the speed of the descending weight increases. Method (*a*) illustrates by analogy the growth of electric current in a coil of constant inductance when connected to a battery. In all three types of motion, partition of the activity of the driving weight between change of kinetic energy and "heat-loss," or changes in internal configuration are shown by the model. As far as experiments have been made, there is satisfactory agreement between measurements and the results of mathematical analysis.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF CALIFORNIA.

## 12. RESTRICTION OF THE ELECTRON BEAM FROM THE HOT CATHODE BRAUN TUBE.

BY L. T. JONES AND H. G. TASKER.

THE usual method is to direct an unrestricted beam from the incandescent cathode against the anode, a small hole in the anode determining the size of the beam. In the present method the anode is an annular ring. A disc with a central hole of about 1 mm. is placed immediately in front of the hot filament, the plane of the disc perpendicular to the axis of the tube. A few volts between this disc and the filament carries the electrons through the hole in the disc, the larger voltage between disc and anode carrying the beam down the tube. The proper adjustment of voltages and dimensions assures a narrow beam down the axis of the tube.

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## 13. A CONSTANT RESISTANCE UNIVERSAL SHUNT.

BY H. G. TASKER.

THE Ayrton-Mather[1] universal shunt for galvanometers provides a multiplying factor $n$ which is independent of the galvanometer resistance, but the effective resistance of the circuit varies widely with $n$. The new circuit eliminates this variation, while retaining the advantages of the former circuit.

The usual Ayrton shunt is connected to a similar circuit through resistances $b_1$, $b_2$, etc., corresponding to values of $n$. A resistance $r_3$ occupies a circuit position corresponding to that of the galvanometer. If $r$ be the total resistance shunting the galvanometer and $r_2$ the corresponding resistance in the added circuit, any values may be chosen for $r$, $r_2$, $n$ and the galvanometer resistance $R$ consistent with the ranges desired, whereupon

$$b = r_2 + \frac{r}{n^2} - \frac{r}{n} - \frac{r_2}{n},$$

$$r_3 = \frac{r^2}{R^2} + \frac{r^2}{r^2} - r_2.$$

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## 14. THE STANDARDIZATION OF PERMANENT MAGNETS.

BY RICHARD HAMER.

FOR an investigation on the "ageing of so-called permanent magnets" used in wattmeters, signal devices and electrical meters, it was necessary to devise an expeditious method which would yield results accurate to a hundredth of one per cent. instead of the usual several per cent. The writer succeeded by adopting a null method. The total magnetic flux of a so-called permanent magnet was cut by a falling coil. The current generated was opposed by that from a coil simultaneously cutting the flux of a solenoid carrying an accurately adjusted current. Thus the difference in flux only caused the resultant current through the fluxmeter, and by calibrating the fluxmeter scale an exact balance was not necessary. Due precautions against thermal and magnetic interferences had to be taken. Serious trouble arose because the magnetic distributions for magnets and solenoid are not the same, causing instantaneously unbalanced currents. To reduce the displacement of the fluxmeter coil two methods were proposed, either relating the coil movements so that the peaks of temporary currents coincided, or the use of a cam controlling the relative coil velocities so that both time curves of the temporary currents were of the same type. By accelerating the motion, the first was found sufficient even when the suspension was changed to silver to increase the sensitivity.

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[1] W. E. Ayrton & T. Mather, Electrician, Vol. 32; 1893-4; P. 627.

## 15. THE EFFECT OF TEMPERATURE CHANGES ON THE VISCOSITY OF RUBBER COLLOIDS.

BY RICHARD HAMER.

THIS work was undertaken at the University of Toronto for the Scientific and Industrial Research Council of Ottawa. The varieties of rubber were: Kassai, Cancho, Fine Para, Smoked Sheet, Pale Crepe, and Esmeralda, with viscosities ranging from one to three times that of Benzol. The viscosity relative to Benzol was measured at 30° C. before and after temperature changes which consisted of cooling to 6° C., in freezing solid at 0° C., or at − 190° C. by liquid air, or in heating up to 60° C. Cooling the colloidal solutions seemed to cause a slight increase. Freezing solid caused a greater increase. Heating seemed to bring about a slight increase. These results depended apparently on the variety and the concentration. Successive applications appeared to have a cumulative effect, indicating, however, a limiting value. There was a slow recovery with time to the original or an even lower value. This is evidently a sort of hysteresis effect and is remarkably similar to that secured on stretching a piece of vulcanized rubber. It is suggested that temperature changes, particularly freezing solid, cause a temporary polymerization of the rubber molecules. The molecular aggregate is, however, unstable and the forces in solution result in a later depolymerizing action which lasts until equilibrium is reached again.

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